MANUFACTURE OF SODA

With Special Reference to the Ammonia Process

A Practical Treatise

By

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American Chemical Society
Monograph Series

IN MEMORIAM

Professor Daniel Dana Jackson
A Dear Friend and Kindly Teacher
To Whose Inspiration I owed in
Large Measure the Writing of this
Second Edition of My Book

GENERAL INTRODUCTION

American Chemical Society Series of
Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, secretary of the society, Washington, D. C.; the late John E. Teeple, then treasurer of the society, New York; and Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the A. C. S. series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successors) of New York.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed editors (the present list of whom appears at the close of this introduction) to have charge of securing authors, and of considering critically the manuscripts submitted. The editors endeavor to select topics of current interest, and authors recognized as authorities in their respective fields.

The development of knowledge in all branches of science, especially in chemistry, has been so rapid during the last fifty years, and the fields covered by this development so varied that it is difficult for any individual to keep in touch with progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and by such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie, Moissan's Traité de Chimie Minérale Générale, Friend's and Mellor's Textbooks of Inorganic Chemistry and Heilbron's Dictionary of Organic Compounds, it often takes a great deal of time to coördinate the knowledge on a given topic. Consequently when men who have spent years in the study of important subjects are willing

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to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value. It was with a clear recognition of the usefulness of such work that the American Chemical Society undertook to sponsor the publication of the two series of monographs.

Two distinct purposes are served by these monographs: the first, whose fulfillment probably renders to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a form intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs enable such men to form closer contact with work in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well-digested survey of the progress already made, and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, extended references to the literature enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection is made of those papers which are most important.

Foreword

The first edition of "Manufacture of Soda" was written in my home. I count it a privilege, therefore, to be asked by the author, whom I have known for almost thirty years, to write this Foreword to the Second Edition of his valuable contribution to chemical technology.

I know of no person so eminently fitted for writing on the subject as Dr. T. P. Hou. Dr. Hou is not only a scholar by training but also an engineer and technologist with years of experience in building up China's chemical industries. To him China owed the first and one of the largest alkali plants in the Far East. This was located in Tangku near Tientsin. When fighting began at the Marco Polo Bridge in July, 1937, just a short distance from the plant, it had attained a daily production capacity of some three hundred tons of soda ash, which was a good record on the Continent of Asia.

To him China also owed her new Synthetic Ammonia industry. Having established the alkali industry in North China, Dr. Hou turned to the great Yangtze Valley to erect the first and largest nitrogen fixation plant in China. Dr. Hou personally supervised the building of the four modern chemical plants at Hsiehchiatien near Nanking, which took three years to complete. In the summer of 1937, the plants were producing 150 tons of ammonia sulfate daily, and the Chinese farmers, sold on the new fertilizer, had booked orders a year ahead. Soon the War of Invasion broke out, interrupting the work.

I was so impressed with the transformation of the farming village of Hsiehchiatien into a humming industrial town, equipped with modern chemical machinery, that on one of my visits to my homeland I had the American Ambassador, Nelson T. Johnson, and the president of the Export-Import Bank, Warren Lee Pierson, accompany me on a tour of inspection. The statesman and the banker were both pleasantly surprised and impressed.

Time marched on . . . . When bombs were falling thick and fast, and when his associates urged him to leave the plants, Dr. Hou said: "My duty to the farmer is to stay on the job. I want to see it through." Dr. Hou caught the last boat to leave Nanking with time to save nothing except a roll of blue prints of the plants. Dr. Hou's contributions are continuing, for far into the interior of Free China he is laying the groundwork for a new chemical industry, despite the difficulties of transportation over the tortuous Burma Road.

It is against such a background that the author was requested by his publishers to prepare this Second Edition of "Manufacture of Soda." It is my privilege to say that he has not spared himself one bit in the

rewriting and revising of this treatise. When the first edition appeared, it was the first of its kind to appear in the English language. In bringing the book up to date and adding considerable new material, Dr. Hou has not only enhanced its usefulness but he has shown the public how an interesting and comprehensive treatise can be written on such a special subject as the Ammonia Soda industry.

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Chapter 1

Introduction. Historical Survey of Alkali Industry and Relation of LeBlanc Soda Industry to Development of Other Chemical Industries

We shall first discuss the LeBlanc process and its historical relation to the development of other chemical industries. In the early part of their work students of elementary inorganic chemistry come across such processes as the Weldon process, the Deacon process, and so forth; but probably they do not realize the close bearing of these processes on the LeBlanc soda industry. In the discussion which follows, the development of the LeBlanc soda industry will constitute a historical treatment of the early chemical industries with the LeBlanc process as their nucleus. With the passing of the LeBlanc process as an active method for the manufacture of soda, most of these industries must necessarily also pass into oblivion; but the foundation laid by the LeBlanc soda industry in paving the way for the more modern chemical industries is well worth consideration.

The artificial soda industry originated in France, but for its development and application we must turn to England. France, as a leading nation in Europe in the Eighteenth Century, consumed considerable quantities of soda annually. While she was engaged with England in the so-called "Seven Years' War" and with practically all Europe in the Napoleonic wars, the source of Spanish barilla was closed to her. She had to find some way to get soda. In 1775 her Academy of Science offered an award of 2400 livres for the invention of a practical process for the manufacture of soda. It was known in a vague way before this time, that soda could be made from common salt, for, in 1773, Scheele was able to get some caustic soda by digesting litharge in strong brine according to the following reaction:

$$2NaCl + H_2O + xPbO \rightleftarrows 2NaOH + [(x-1)PbO] . PbCl_2$$

where $x = 2, 3, 4$ or 5 according to the concentration of the brine. The filtrate of brine from the mixture of PbO and $PbCl_2$ contains some caustic soda, and the conversion decreases as the temperature employed is raised, owing to the greater solubility of $PbCl_2$ at a higher temperature..

Among several methods presented, there was one by Nicolas LeBlanc (1742-1806), who outlined a method of manufacture starting with common salt. His process was so promising that in 1783 the French Academy

of Science promised to award him the prize. It was, however, never given to him. He obtained a patent in 1791, and, being physician to the Duke of Orleans, he received 200,000 livres from him for the construction of a plant in St. Denis, not far from Paris. In 1793, the Duke was guillotined by the French Revolutionists. Being desperate to obtain soda, the Committee of Public Safety of the Revolutionists' Government compelled LeBlanc to make his patent public without remuneration except by assigning to him the St. Denis Works from the confiscation of the Duke's property (Fig. 1). Deprived of his working capital, LeBlanc could not
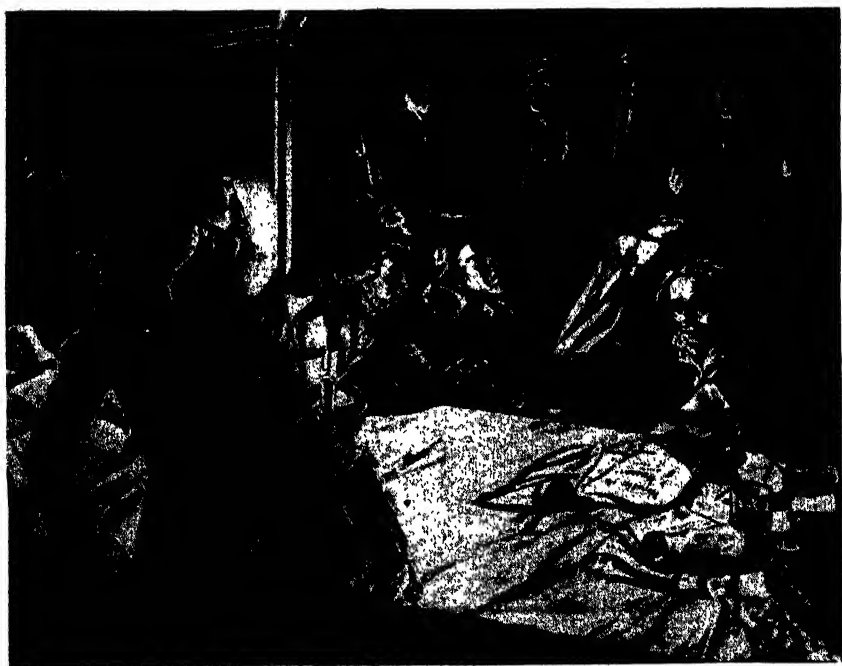
Fig. 1. LeBlanc forced by French Tribunal to make his patent public.

operate the works and was forced to shut it down. He had to spend the latter part of his life in an almshouse where, in his misery, he committed suicide in 1806. Thus ended the life of a man whose invention was of such great value to the world. His original proportion of 100 pts. by weight of salt cake: 100 pts. of limestone: 50 pts of coal was only slightly modified to 100 pts. of salt cake: 100 pts. of limestone: $35\frac{1}{2}$ pts. of slack coal, in the course of the long period of its application. All improvements that were subsequently made on his process had to do with mechanical equipment. Rarely has there been a process so nearly perfect in form as that first discovered by LeBlanc. In spite of the fact that he was the founder of a process so beneficial to mankind and so lucrative to people who employed his process, LeBlanc himself died poor and unknown. His

country was not benefited by his discovery to the extent that it might have been, and his name was for the time even forgotten by his own countrymen. It was not until 1886, after millions of tons of soda ash had
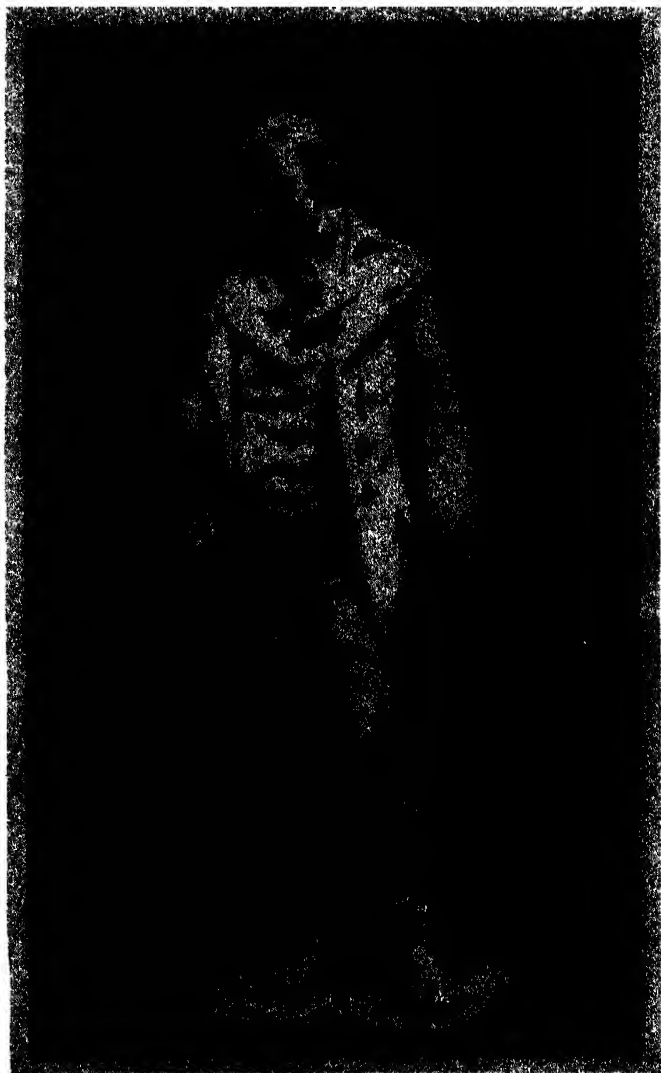
Fig. 2. LeBlanc statue in Paris.

been made in England and Germany by the LeBlanc process, that they began to erect a statue in his honor at the Conservatory of Arts and Trades in Paris (Fig. 2).

Because of the prolonged wars into which France had been plunged,

the soda industry, like many other industries, could not be developed to any extent. In England it had a better chance, although the Napoleonic wars left England impoverished like many other European countries. From the time when peace was declared at the Congress of Vienna in 1815, she had to levy a very heavy tax of £30 per ton on salt. Under this tax, it would have been impossible for her soda industry to exist. After eight years, however, the British government wisely decided to repeal the law, and the year 1823 saw the tax removed. From this time on, the soda industry went ahead by leaps and bounds quite in contrast to the conditions in France. James Muspratt (1793-1886), an Irishman, who had served as an apprentice in a fine-chemical factory, first started a sulfuric acid industry at Liverpool in 1822 and then, taking advantage of the tax exemption on salt, built a LeBlanc soda plant there in 1823. The undertaking proved profitable. After enlarging his plant to its fullest extent, he built a second LeBlanc soda plant at Newton, which was later removed to Widnes, and subsequently a third LeBlanc soda plant at Flint. Meanwhile other LeBlanc soda plants also sprang up at Widnes, St. Helens, Runcorn, the Tyne, Glasgow, and in other districts, where the necessary raw materials, sulfur, salt, limestone and coal, were available in abundance. Thus, the great development of the LeBlanc soda industry in Great Britain was made possible by the repeal of the salt tax in 1823.

The period from 1825 to 1890 saw the LeBlanc process occupying a leading position. All artificial soda was made, and made in large quantities, by this process. In 1861 Ernest Solvay (1838-1922) rediscovered and perfected an old process now known as the ammonia soda process. In 1863 with his brother Alfred he constructed a works at Couillet, Belgium, near Charleroi, which began to operate in 1865, using this process. Only after encountering a series of serious difficulties, which threatened to bring failure to his undertaking, did he finally make a success of it. The works was gradually improved, enlarged, and remodelled. In 1872 the capacity was brought up to 10 tons of soda ash a day, which proved to the world the success of his process beyond any doubt. In that year he designed a large soda plant at Dombasle near Nancy, France, on a scale considered quite gigantic at that time. Dr. Ludwig Mond, an old LeBlanc soda man, came over to visit Solvay, with the result that the latter's process was allowed to be introduced in England. Brunner, Mond & Co. was then formed and the first works erected at Winnington, near Northwich, England, in 1874.

Like the LeBlanc soda industry, the ammonia soda industry developed by leaps and bounds. The new soda industry, however, had not only to meet many difficulties inherent in its operation but also to meet competition from the well-established LeBlanc soda process. However, it was able to hold its own in the face of competition, because of the simplicity of raw materials needed, of the low cost of production, and of the very high purity of the soda ash produced. From about 1885 on, the curve of LeBlanc soda production began to take a downward course as the result of competition from the new process. The price of soda ash

declined from some £13 per ton to little more than £4 per ton. The LeBlanc soda manufacturers had to dispose of their soda at a loss and to make up the loss from the sale of bleaching powder. The Bleaching Powder Association was then formed in England as an organ of the LeBlanc soda manufacturers to maintain the market price of bleaching powder. In 1890 this culminated in a then colossal combine of practically all LeBlanc soda interests in Great Britain into one company known as The United Alkali Co., Ltd., consisting of forty-eight works (45 chemical and 3 salt works), of which 42 were in England, 4 in Scotland and one each in Ireland and Wales. From this, some idea can be obtained as to how deadly the struggle was between the new and the old processes. Heretofore, there had been a certain definite balance between the quantities of soda and bleaching powder produced. With the advent of the ammonia soda process, only the alkali was produced without its counterpart in chlorine. This balance was disturbed, and it was difficult for LeBlanc soda manufacturers to adjust themselves to meet the new situation.

Despite this huge combine, the position of LeBlanc soda was still untenable. To avoid direct competition, The United Alkali Co. turned its attention to the manufacture of other chemicals, such as sulfuric acid, muriatic acid, bleaching powder, etc., starting from pyrites as raw material. Meanwhile, Brunner, Mond & Co. grew to a position of mastery in the soda trade of England. Just as James Muspratt took over LeBlanc's process and developed the LeBlanc soda industry to the greatest benefit of England, so Ludwig Mond introduced Solvay's process and developed the ammonia soda industry to such an extent that Brunner, Mond & Co. (at present merged into Imperial Chemical Industries, Ltd.) controls the soda market not only in England but also in many parts of the world, through the export of its large surplus of soda ash.

While the LeBlanc process for soda ash was forced to decline, its use for caustic soda manufacture possessed some advantages. First, the soda liquor from the lixiviating vats could be used directly for causticization, and secondly, the lye as obtained already contained as much as 20 per cent of the causticity of the total alkali present, so that only 80 per cent of the normal amount of lime was required for causticization. With the advent of the electrolytic process, however, another serious blow was dealt to the LeBlanc process. Here in one operation were obtained chlorine and caustic soda—and these in a pure and concentrated form—while these two main products of the LeBlanc process were obtained only after a considerable number of intricate steps.

From 1890 on, the LeBlanc process suffered a rapid decline. The World War (1914-1918) found the position of the LeBlanc process for soda manufacture still untenable. Because of the demand for sulfuric acid for the manufacture of munitions, and because of the threatening shortage of coal, the British Government during the War imposed restrictions on the use of these important raw materials. The LeBlanc soda works was hard hit, and in 1915-1916 The United Alkali Co. practically stopped making soda by this process. The Company then became engaged instead

in making concentrated sulfuric acid, picric acid, poisonous gases, and other war chemicals for the British Government. ·

After the war, the chemical industries had to readjust themselves. Competition among the different nations for the world market was resumed with even greater vigor. Efficiency was the watchword; and the LeBlanc process, which involved much labor, high cost of manufacture, low purity, and a complex line of products, had to give way to a newer, more efficient process. In 1923, The United Alkali Co. decided to scrap the last portion of its LeBlanc soda equipment, and the death verdict for the LeBlanc process for soda ash manufacture was finally delivered. On the European continent similar conditions occurred, although the remnants of the LeBlanc process in many places did not even survive up to the War. Born of necessity during the War in France and superseded because of the necessity caused by the World War I, the LeBlanc process, which had served mankind for fully a century, had completely fulfilled its mission. We shall now dwell at some length upon the relationship between the LeBlanc soda industry and the other chemical industries.

Though the LeBlanc process was discontinued, LeBlanc soda works remained. The United Alkali Co. in England became engaged in the manufacture of various heavy and fine chemicals. The change consisted merely in replacing the LeBlanc process for soda manufacture by the ammonia process at Fleetwood. And now this United Alkali Co. became indeed the largest manufacturers of sulfuric acid in England, as if the name of the company were a misnomer. The reason is to be found in the nature of the LeBlanc process. It requires for one of its principal raw materials salt cake, or sodium sulfate, which in turn has to be made from common salt by treatment with sulfuric acid. Thus, sulfuric acid indirectly becomes its important raw material. The LeBlanc soda manufacturers generally made their own sulfuric acid. Thus we find that they were also large manufacturers of sulfuric acid (chamber acid). From salt and sulfuric acid are obtained salt cake and hydrochloric acid, which latter is in itself a valuable chemical. Hence we find that LeBlanc soda manufacturers are necessarily manufacturers of hydrochloric acid. As the muriatic acid as such did not find much use at the earlier time, most of it was converted to chlorine; from this, bleaching powder was made which found very extensive application in the textile and paper industries. Thus, the bleaching powder industry was necessarily connected with the LeBlanc soda industry. The salt cake required by glass manufacturers was also supplied by LeBlanc soda manufacturers. The CaS residue known as "tank waste" proved to be quite a nuisance, for there was so much of it that its disposal became a problem. For every ton of soda ash produced there were more than $1\frac{1}{2}$ tons of this waste left. So foul was its odor and so objectionable was the pollution of surface water by it that its proper disposal became a matter of no small concern to the community. Added to this was the fact that it contained all the sulfur originally present in the sulfuric acid. The recovery of sulfur was finally worked out and exceptionally pure sulfur was obtained as another by-

product. The high price of sulfur, largely due to taxation, induced the soda manufacturers to seek a cheaper source of sulfur, and pyrites were employed, not only for its sulfur but also for the iron and copper contained in it. Here, then, a group of important products were obtained: namely, sulfuric acid, hydrochloric acid, salt cake for the glass industry, bleaching powder for the textile and paper industries, sulfur, and lastly iron and copper—all clustered together around this LeBlanc soda industry.

Of great interest to students of chemical engineering was the apparatus developed in connection with the LeBlanc process. The hydrochloric acid fumes from the salt cake process discharging to the air through the chimney worked havoc on the vegetation in the vicinity. The British Government had laws known as Alkali Acts (1863, 1874), restricting the content to within 2 grains HCl per cu. ft. A coke-packed washer was invented to scrub the gas. This washer was the basis of all types of scrubbers now used in other branches of the chemical industry. In the black ash process, a revolving furnace called the "revolver" took the place of the old hand-operated furnace. This cut down the strenuous labor required of the furnace workmen and greatly increased the output. This "revolver" may be called the forerunner of the present rotary kilns employed in one style or another in so many furnacing operations. In the final drying of the monohydrate $Na_2CO_3 . H_2O$ for soda ash, and also in the salt cake process, a mechanical furnace with a revolving bed, called McTear's furnace, was employed. For evaporating (or concentrating) the black ash liquor, and for crystallizing the monohydrate, an open Thelen pan with revolving scrapers did away with much difficulty arising from scale formation at the bottom of the pan by the monohydrate. Without efficient stirring, a hard scale would be formed in the pan, causing the iron shell to be burned out. This Thelen pan in its closed form, which had oscillating, instead of revolving scrapers, was later introduced into the ammonia soda industry in England for calcining the bicarbonate and for recovery of the CO_2 gas. Likewise, McTear's mechanical furnace was introduced for finishing soda ash or for making dense ash in the ammonia soda industry. Even up to the present time, some ammonia soda works are still using these pieces of machinery, especially in European practice. Finally, the Shank lixiviating system for black ash liquor embodied the counter-current principle that has been so widely applied in dealing with leaching and extraction processes in all modern chemical industries. All these important pieces of apparatus and some minor ones not mentioned above, our young modern chemical industries owe to the old LeBlanc soda industry.

The LeBlanc soda industry produced a number of brilliant men whose contribution to chemical technology, either in the discovery of a chemical process or in the invention of chemical equipment, laid the foundation for many modern chemical industries. These men helped to make the LeBlanc soda industry what it was. The very difficulties these pioneers encountered and their methods of attack solved once for all, or offered solutions to, similar problems arising in other branches of chemical indus-

try. In the early salt cake process, hydrochloric acid fumes were allowed to discharge into the atmosphere through a chimney, and heavy damages were collected from these manufacturers. William Gossage in 1836 introduced a coke-packed scrubbing tower for these fumes. The tower was built of sandstone slabs, boiled in tar and clamped together with steel straps. Water was sprayed from the top and trickled through the coke to absorb the upgoing fumes. The apparatus was primarily devised to prevent the escape of acid fumes to the air without any idea of recovering any useful product. But it recovered a valuable product which was one of the factors that prolonged the life of the LeBlanc process in the face of a strong competition from the ammonia soda process.

The market for hydrochloric acid at that time was not very strong, but there was a great demand for bleaching powder. The bulk of the hydrochloric acid had to be converted to bleaching powder. In doing so it was necessary to convert the hydrochloric acid first to chlorine gas. The usual method then in use was to oxidize it with manganese dioxide (pyrolusite) according to the following reaction:

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

It is thus evident that the manganous chloride resulting from the reaction was no longer useful for the work. Further, one-half of the chlorine was not made available this way. The consumption of manganese dioxide also was a considerable item of expense. Walter Weldon from 1866 to 1870 devised a process for the oxidation of manganous chloride to manganese dioxide by means of lime, thus effecting its recovery. The process which bears his name consisted in treating the still liquor with lime, heating it to 55°-60° C. by steam in the presence of excess lime, and blowing in air. Thus, almost all the manganese was recovered in a useful form, and a strong calcium chloride liquor resulted, from which calcium chloride powder could be manufactured rather economically for use in refrigerating plants.

So far as the utilization of chlorine was concerned, oxidation by manganese dioxide made available only one-half of the total available chlorine as mentioned above, with an efficiency of only 50 per cent. Besides, manganese dioxide was recovered in the form of calcium manganite, $CaMn_2O_5$, which consumed acid to free the MnO_2 from CaO. An improvement on this method was discovered by Henry Deacon of the firm of Gaskell, Deacon & Co., Widnes, in 1870, who used oxygen direct from the air for oxidation in the presence of copper chloride ($CuCl_2$) as a catalyst. Though the chlorine gas obtained was rather dilute and demanded a special apparatus for the manufacture of bleaching powder, all the chlorine present in the manganese chloride was made available, and, further, the excessive alkalinity due to CaO was avoided.
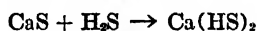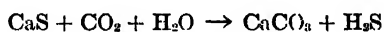
The process for making bleaching powder from chlorine gas and lime, which then took so much hydrochloric acid from the LeBlanc process manufacturers, was discovered by Charles Tennant, a Scotch merchant,

who, in 1788, first made a solution of "chloride of lime." Later he developed a solid powder. The chloride of lime bleached cloth in a few hours and accomplished what bleaching in the sun's rays could only do in months. In 1797 Tennant set up a chemical works in St. Rollox, Glasgow, and in 1799 he received a patent for making solid chloride of lime, to which he gave the name "bleaching powder." This so revolutionized the textile industry that bleaching powder became an important article, and considerable hydrochloric acid from the LeBlanc process was converted into chlorine for the manufacture of bleaching powder.

In the LeBlanc process the black ash, after leaching, left a residue known as "tank waste." The waste began to accumulate so fast (about $1\frac{1}{2}$ tons for every ton of soda ash made) that its disposal became a serious problem. Here came Dr. Ludwig Mond (1862), who made use of air oxidation to free the sulfur. This is Mond's process for the recovery of sulfur from tank waste. The name of Mond is, however, usually associated with the development of the ammonia soda industry in England, though he was originally one of the LeBlanc soda men. His work in the development of the ammonia soda industry has overshadowed all this. At the same time another promising process was proposed by Schaffner, who used magnesium chloride in conjunction with air:

$$2CaS + 2MgCl_2 + O_2 \rightarrow 2CaCl_2 + 2MgO + S_2$$
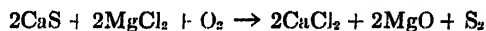
The one process that was used successfully on an extensive scale, however, is that known after its inventors as the Chance-Claus process. In this process the waste was treated with carbon dioxide gas in a battery of carbonators whereby hydrogen sulfide gas was liberated and calcium sulfide transformed into calcium carbonate according to the following reactions:

$$CaS + CO_2 + H_2O \rightarrow CaCO_3 + H_2S$$
$$CaS + H_2S \rightarrow Ca(HS)_2$$
$$Ca(HS)_2 + CO_2 + H_2O \rightarrow CaCO_3 + 2H_2S$$

The hydrogen sulfide gas was burned to free sulfur by means of a carefully regulated supply of air in the presence of hydrated iron ore (ferric oxide) as a catalyst, thus:

$$2H_2S + O_2 \rightarrow 2H_2O + S_2$$
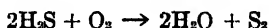
The sulfur reclaimed from the tank waste is in a very pure form. It is thus possible to reclaim from the crude sulfur originally present in the pyrites that went to make sulfuric acid, pure free sulfur, commanding a good price on the market.

In connection with the burning of pyrites for sulfur dioxide gas, an iron oxide rich in copper resulted. Longmaid and Henderson devised a method of extracting copper from it by calcining it with salt, leaching out the copper chloride, and precipitating copper with iron scrap. This is known as the Longmaid and Henderson Wet Copper Process.

In an attempt to manufacture soda by LeBlanc's process without starting from sulfuric acid as one of the raw materials, Hargreaves in 1870 discovered a method of making sodium sulfate directly from sulfur dioxide and common salt. A mixture of sulfur dioxide, air, and steam is passed through layers of especially prepared salt blocks at a temperature of 400-500° C., when the following reaction takes place:

$$4NaCl + 2SO_2 + 2H_2O + O_2 \rightarrow 2Na_2SO_4 + 4HCl$$
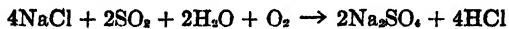
This is known as the Hargreaves process. As usual, hydrochloric acid is formed in the reaction, but without the use of sulfuric acid. In this country at present, because of the large demand for sodium sulfate for kraft paper manufacture and because of the introduction of the synthetic method for manufacturing hydrochloric and nitric acids, certain attempts have been made to revive the Hargreaves process for the production of sodium sulfate, which was formerly a by-product from the treatment of salt or Chile saltpetre with sulfuric acid for the production of hydro- chloric or nitric acid.*

All these processes were developed from the necessities of the LeBlanc soda industry, and their inventors were really pioneers in the application of chemical principles to industry, laying the foundation of what is now known as the chemical technology of heavy chemicals.

Although the LeBlanc process for soda ash manufacture has now been given up in favor of the newer ammonia process, the development of the sulfuric acid industry on the one hand, and the production of hydro- chloric acid, bleaching powder, etc., on the other, are the direct outcome of the LeBlanc process. Heavy-chemical industries in general are lucky enough to have had a start in the LeBlanc industry. For, unfortunately or fortunately, the LeBlanc process involves the manufacture of all these chemicals, and what were originally by-products later became the prin- cipal products. It can be truly said that the history of modern inorganic chemical industry owes its beginning to the LeBlanc soda industry.

For the sake of clearness to the reader, the diagram in Fig. 3 is given to show how varied were the products from the LeBlanc industry. Products enclosed in rectangles were those appearing in commerce.

In contrast with these older methods, it may be mentioned briefly by way of digression that modern methods utilize these waste sulfur gases from pyrites roasters for the manufacture of concentrated sulfuric acid, not by the chamber process but by the vanadium contact process. For this purpose, mechanical roasters such as the Herreshoff furnace, the Wedge furnace, etc. are used, and the gases from these roasters are main- tained at 7 per cent or higher SO_2 by volume. This strength of sulfur gas is adequate for efficient conversion by the vanadium mass for the manu- facture of contact acid. The waste gases are settled, cooled, and scrubbed by passing through an elaborate purification sytsem to remove dust and

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*A synthetic "sulfate" of soda plant was erected in Lake Charles, La., for the manufacture of sodium sulfate by fusing soda ash and elemental sulfur in molecular proportions.

moisture, led through a wet Cottrell system to remove SO_3 mist, and finally dried through a drying tower. The dried and cleaned gas is then passed into the vanadium contact mass through a system of heat exchangers. From the vanadium converters, the gases are led through

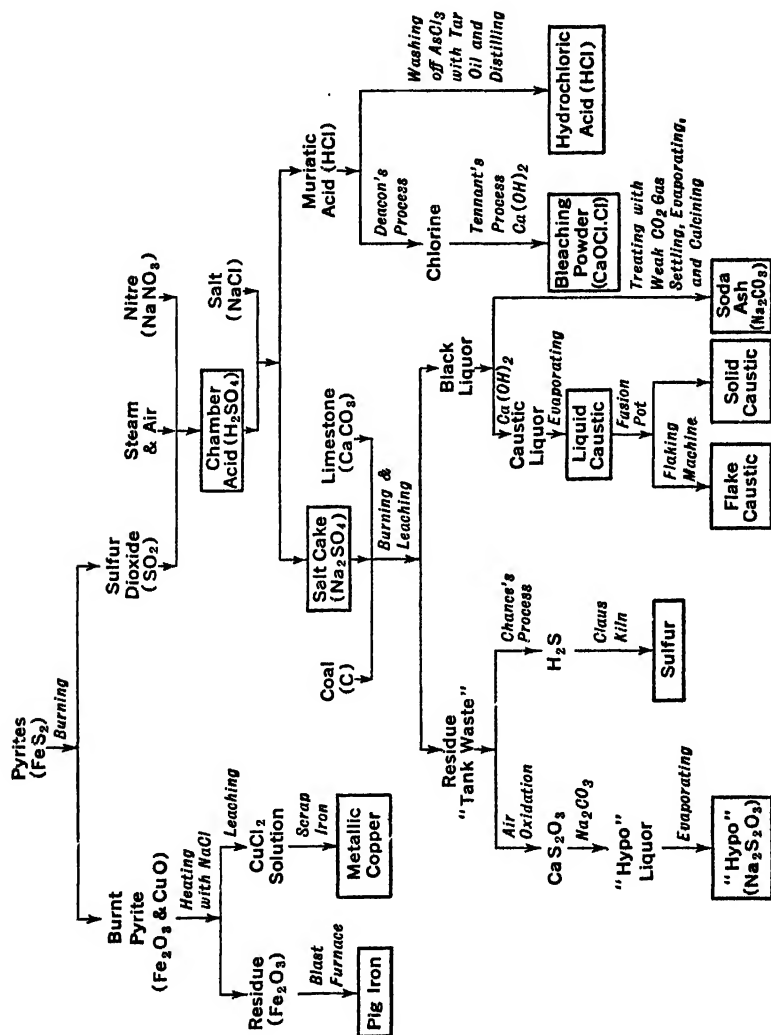Fig. 3. Diagram of LeBlanc soda industries.
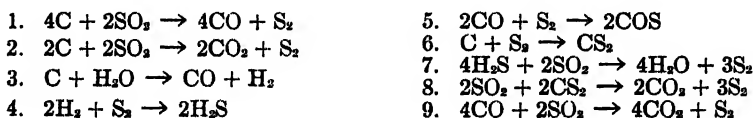
absorption towers to make 98-99 per cent H_2SO_4 or 105-109 per cent oleum.

If the utilization of such waste gases for the manufacture of sulfuric acid is not sufficient to take care of all the gases available, due perhaps to the limited demand for sulfuric acid in the country, the remaining waste gases may be converted to elemental sulfur, not by the LeBlanc proce-

dure, but by a direct catalytic reduction. This has been done in many modern plants, *e.g.*, in that of the Consolidated Mining and Smelting Co., Trail, B. C.

For this recovery of sulfur, the present reduction method of SO_2 gas to elemental sulfur proves far superior to the old Chance-Claus process described above. Briefly, there are at present two main processes for the recovery of sulfur from the waste gas. These are the I.C.I. and the Boliden processes.[*] The I.C.I process involves first concentrating the SO_2 gas from the waste gas, purifying the gas, and then liquefying it to liquid sulfur dioxide; or, alternatively, reducing it to elemental sulfur by the water-gas method with the help of a catalyst. Concentration of the gas is achieved by the absorption of the weak gas in a basic aluminum sulfate solution, having a pH value of 3.5, or 40 per cent basicity, the solution containing a small percentage of phosphoric acid as a stabilizer to help keep the Al_2O_3 in solution. Regeneration of SO_2 gas is then effected by the liberation of SO_2 from the basic aluminum sulfate solution by boiling at about 100 °C. As the SO_2 gas has a tendency to be oxidized to SO_3 in the presence of oxygen, pulverized limestone or lime is used to neutralize the acid formed so as to maintain the proper pH value in the solution.

Gaseous sulfur dioxide is reduced by passing it through a water-gas generator at 1200° C., whereby many complex products are formed, as shown by the following equations:

1. $4C + 2SO_2 \rightarrow 4CO + S_2$
2. $2C + 2SO_2 \rightarrow 2CO_2 + S_2$
3. $C + H_2O \rightarrow CO + H_2$
4. $2H_2 + S_2 \rightarrow 2H_2S$
5. $2CO + S_2 \rightarrow 2COS$
6. $C + S_2 \rightarrow CS_2$
7. $4H_2S + 2SO_2 \rightarrow 4H_2O + 3S_2$
8. $2SO_2 + 2CS_2 \rightarrow 2CO_2 + 3S_2$
9. $4CO + 2SO_2 \rightarrow 4CO_2 + S_2$

Catalytic action will convert all these complex products to elemental sulfur. The catalyst consists chiefly of ferric oxide and aluminum oxide. By this process either liquid sulfur dioxide or elemental sulfur can be obtained.

The Boliden process, independently worked out by Swedish research chemists, is a direct reduction of the waste gas into sulfur in one step without concentration or purification of the SO_2 gas. This process is particularly suitable for the manufacture of sulfur directly from the waste gas, where reasonable control of the smelter gas is possible to keep the SO_2 content above 5 per cent.

These two processes of recovering sulfur from waste SO_2 gases are so efficient nowadays that it is possible to recover sulfur of high purity from the waste gases from roasters or smelters, comparable in quality with Louisiana and Texas sulfur.

Other processes, such as McCluskey's process,[†] etc., are all based on

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[*] See article by M. P. Applebey entitled "The Recovery of Sulphur from Smelter Gases," *Journal of Society of Chemical Industry*, May, 1937.

[†] McCluskey, S. B., B. P. 421,289; 421,290; 417,276.

the reducibility of SO_2 by solid carbon or carbon monoxide or water gas products according to the following reactions:

$$2C + 2SO_2 \rightarrow 2CO_2 + S_2$$
$$4CO + 2SO_2 \rightarrow 4CO_2 + S_2$$
$$4H_2 + 2SO_2 \rightarrow 4H_2O + S_2$$
$$CH_4 + 2SO_2 \rightarrow CO_2 + 2H_2O + S_2$$
$$2C_2H_4 + 6SO_2 \rightarrow 4CO_2 + 4H_2O + 3S_2$$
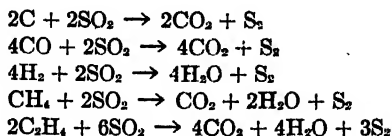
along with many side reactions. These reactions are carried out in the presence of a catalyst. Various catalysts have been suggested, and even solid charcoal in the water gas generator may be considered as such a catalyst.

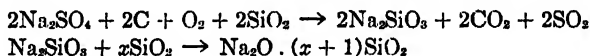In summarizing, we might add that in England and on the continent, LeBlanc's process for soda manufacture has now disappeared, while in the United States, soda ash from the very beginning has been made exclusively by the ammonia process. At present, one part of the LeBlanc process is left in the form of hydrochloric acid manufacture:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$
$$NaHSO_4 + NaCl \rightarrow Na_2SO_4 + HCl$$
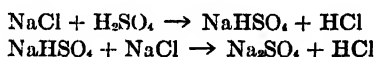
and another, leaving out the limestone, is used in the manufacture of sodium sulfide:

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$$
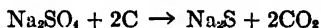
A slightly modified form, with the addition of pure quartz sand in place of limestone, is employed in the water-glass manufacture:

$$2Na_2SO_4 + 2C + O_2 + 2SiO_2 \rightarrow 2Na_2SiO_3 + 2CO_2 + 2SO_2$$
$$Na_2SiO_3 + xSiO_2 \rightarrow Na_2O \cdot (x + 1)SiO_2$$

But the complete process for the manufacture of soda ash has sunk into oblivion. In the matter of purity, cost of manufacture, labor involved in handling, and simplicity in the line of products obtained, LeBlanc's soda process cannot compete with the ammonia process. And for the production of caustic soda and bleaching powder, the present electrolytic method possesses every advantage: nobody nowadays would think of manufacturing bleaching powder from hydrochloric acid through the many intermediate stages represented by the Weldon or Deacon process. Indeed, the increased demand for chlorine has greatly spurred electrolytic production to such an extent that the quantity of caustic soda produced as a joint product from this electrolytic method has now equaled or exceeded that produced by the lime process, as will be seen in Chapters XIX and XX.

Chapter II
Natural Soda

Before the advent of the LeBlanc soda process, all soda came from natural sources, either vegetable or mineral. Vegetable soda made from the ashes of certain plants or seaweeds must have been known to the ancients long before recorded history. Primitive people burned the stalks of certain plants to ashes which they leached with hot water, obtaining a brown-colored lye for domestic laundering. Gradually soda from these sources became a staple commodity in commerce, and we hear notably of Spanish barilla at the time of the French Revolution. There were many such commercial varieties from different localities, and they had widely varying alkali contents. Undoubtedly in some cases (such as kelp or varec) the alkali content is potash ("Pot-Ash") rather than soda. These products went under the names of barilla or bourdin in Spain; blanquette, salicor or varec in different parts of the coast of France; and kelp along the Atlantic coast of Great Britain. Their approximate soda contents are given in Table 1.

TABLE 1. Natural Soda from Vegetable Sources (Seaweeds) Before
the Days of LeBlanc.

Place of Occurrence	Name in Commerce	Na_2CO_3* (%)
Southern Spanish Coast (Alicante, Malaga)	Barilla	25–30
Southern Spanish Coast (Cartagena)	Bourdin	20–25
Northern French Coast (Cherbourg)	Varec	3–8
Southern French Coast (Argues-Mortes)	Blanquette	4–10
Southern French Coast (Narbonne)	Soude de Narbonne (salicor)	14–15
†Western Scotch and Irish Coast	Kelp	10–15

* Different authorities give different figures for the soda content. The plant ashes contained from 2 to 40 per cent of their weight of soda.
† At present found also on the coasts of Japan and on the Pacific coast of the United States.

By far the greatest quantity of natural soda comes from mineral sources—so much so that natural soda is now understood to be of mineral origin. Natural soda from mineral sources may usually be identified by its content of more or less varying proportions of sodium bicarbonate and sodium sulfate, whereas artificial (ammonia) soda always contains a small proportion of iron. Natural soda occurs in many places on the surface of the earth. It is usually found (1) in crystalline form as sal soda, $Na_2CO_3 . 10H_2O$, known as natron; (2) in powder form as an efflorescence

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on top of the crystalline mass, mostly as the monohydrate, $Na_2CO_3 . H_2O$, known as thermonatrite; (3) in fine crystalline form as the sesquicarbonate, $Na_2CO_3 . NaHCO_3 . 2H_2O$, known as trona in Egypt or urao in Colombia, Venezuela and Mexico; and (4) in the form of soda brine containing sodium carbonate, sodium sulfate, and sodium chloride among other salts in solution. The deposits are generally found in low valleys where there is little rain and where the air is dry.

The origin of natural soda is rather difficult to determine. It seems that many forces in nature are at work. and in conjunction with local geologic formations, these give rise to peculiar deposits found in different parts of the world. In general, it seems likely that natural soda owes its origin to the decomposition of rocks or soil by the agencies of air, moisture, heat, and pressure, followed by subsequent chemical changes, the products being leached by water, converted to the carbonate by atmospheric carbon dioxide, and concentrated by natural evaporation.* Volcanic activities with their attendant heat and pressure effects have been considered to be one of the most powerful agencies responsible for the decomposition of rocks yielding the soluble salts of sodium (silicate, chloride and sulfate) which are dissolved by water, furnishing raw materials for the subsequent chemical changes mentioned above. The following is an enumeration of the several ways, in one or more of which a particular deposit may have been formed:

(1) From the deposition of soda leached out by water from rocks rich in soda which were undergoing decomposition (as in the case of the old Lahontan Lakes in the State of Nevada).†

(2) From volcanic action and subsequent solution of the volcanic ash by water, giving rise to soda brine (as in Owens Lake, California).

(3) From the decomposition of sodium silicates by atmospheric carbon dioxide setting free silicic acid. (Some of the Egyptian soda is believed to have been thus formed.)

(4) From sodium sulfate which is reduced by organic matter (such as algae) to sulfide, which then is decomposed by atmospheric carbon dioxide forming sodium carbonate and liberating hydrogen sulfide and sulfur. (The natron lakes of Egypt are thought to have been formed in this way.)

(5) From sodium chloride or sulfate which, in contact with limestone, is slowly acted upon by calcium bicarbonate, $Ca(HCO_3)_2$, formed from calcium carbonate and atmospheric carbon dioxide. Double decomposition then takes place, yielding sodium bicarbonate and calcium chloride or sulfate, the sodium bicarbonate giving sodium carbonate by decomposition. This accounts for some of the Hungarian deposits and for the formation of Gay-Lussite, $Na_2CO_3 . CaCO_3 . 5H_2O$ in Taboos-Nor (Kirin), Lagunilla (Venezuela), and certain soda lakes in Carson Desert (Nev.).

From the above it will be evident why natural soda is frequently accompanied by more or less sodium sulfate and sodium chloride. What-

* T. M. Chatard, Bulletin, U. S. Geol. Survey, No. 60, pp. 89-95.
† Moses and Parsons, "Mineralogy, Crystallography and Blow-pipe Analysis," p. 425 (1916).

ever may be the cause, there is seldom one agency alone which brings about the formation of these deposits in the different parts of the world. Often in one locality there is more than one deposit. For example, Gay-Lussite and trona occur together in the Lagunilla Valley, Venezuela.

Natural soda contains considerable sodium bicarbonate, more or less sodium sulfate, some sodium chloride, potassium chloride, borax, and a small proportion of insoluble matter. Crystals are gradually formed from soda brine which becomes concentrated by natural evaporation. During cold weather, crystals of sal soda separate out from solution. By efflorescence, the crystals on the exposed layers crumble to the powdered monohydrate, from which by weathering action under the influence of atmospheric carbon dioxide and moisture, sesquicarbonate or trona results. Such processes continue, so that we may find all three (sal soda, monohydrate, and sesquicarbonate) existing together in the same deposit.

Table 2 is a list of some of the better known deposits.

TABLE 2. Some Better Known Deposits of the World.

Africa	Lower Egypt: Wady Natrun British East Africa: Magadi Lake Former German East Africa: Moshi Libya: Fezzan

The Americas	United States:
	  California: Owens Lake (Inyo County); Searles Lake, Trona (San Bernardino County); Borax Lake (Lake County)
	  Nevada: Ragtown Soda Lakes (near Carson Sink)
	  Wyoming: Union Pacific Lakes, near Green River and along Union Pacific Railroad)
	  Oregon: Abert Lake
	Mexico: Lake Tezcoco
	Venezuela: Lagunilla Valley
	Chile: Antofagasta

Asia	Siberia: Chita and Lake Baikal Region, Barnaul, Slavgorod
	Armenia: Araxes Plain lakes
	India: Lake Looner, etc.
	China:
	  Outer Mongolia: Various "Nors"
	  Sui-Yuan: Cha-Han-Nor, Na-Lin-Nor, Pa-Yen-Nor
	  Heilungkiang: Hailar, Tsitsihar
	  Kirin: Fu-U-Hsien, Taboos-Nor
	  Liao-Ning: Tao-Nan Hsien (Polishan lake, Tafusu lake, etc.)
	  Jehol: Various soda lakes
	  Chahar: Cheng-Lang-Chi
	  Shansi: U-Tsu-Hsien
	  Shensi: Shen-Mu-Hsien
	  Kansu: Ning-Hsia-Hsien
	  Tibet: Alkali deserts

Europe	Russia: Caspian Sea region Hungary: Szegedin district

The list in Table 2 is by no means exhaustive, but it gives some of the better known representative deposits.

Regarding the composition of natural soda, analytical results from different sources vary a great deal. The composition differs with different layers of the same deposit and with varying climatic conditions. Sam-

TABLE 3. Composition of Some Natural Soda Deposits.

	Na_2CO_3	$NaHCO_3$	$Na_2B_4O_7$	Na_2SO_4	$NaCl$	KCl Per Cent	Insoluble	Water	Remarks
* Wady Natrun (Africa)	39	25	....	....	....	....	....	....	Total solid residue containing also other salts
* Moshi (Africa)	45	38	....	....	....	....	....	....	
⊕ Owens Lake Brine (Calif.)	9	1.2	1.0	3	16	1.5	....	74.47	Containing also many other salts
⊕ Searles Lake Brine (Calif.)	4.74	....	1.51	6.96	16.35	4.75	....	65.35	
† Ragtown (Nevada)	45.05	34.66	....	1.29	1.61	....	0.81	16.19	From saline crust containing also $MgCl_2$ 0.67, K_2CO_3 0.27
* Magadi Lake	45.44	33.84	....	....	2.30	....	1.66	16.75	
** Dulla Khar, India	47.55	28.06	....	....	0.60	....	2.65	20.14	
Chinese Natural Soda Samples:									
‡ Barga (Heilungkiang) Lake Soda	28.9	....	....	11.9	....	....	....	58.2	
§ Polishan (Liao-Ning) Lake Soda	12.04	....	....	0.75	1.45	....	....	....	
# Taboos-Nor (Kirin)	34.9	....	....	....	....	....	0.27	30.5	Gay-Lussite containing also $CaCO_3=34.0$ per cent.
Cha-Han-Nor (Sui-Yuan)	42.80	35.51	....	2.20	1.74	....	0.81	16.92	Samples of natural deposit
Pa-Yen-Nor (Sui Yuan)	42.75	10.24	....	6.79	0.54	....	1.20	38.50	Samples of natural deposit
Han-Kai-Chi-Nor (Sui Yuan)	59.90	16.05	....	0.88	0.99	....	Trace	22.18	Samples of natural deposit
Shen-Mu-Hsien (Shensi)	78.32	0.50	....	0.91	4.94	....	0.14	15.00	
U-Tsu-Hsien (Shansi)	53.69	15.52	....	17.33	3.51	....	0.21	11.78	
Kian-Hsien (Kiangsi)	81.48	6.82	....	....	....	....	....	....	

*. J. Kirchner, "Die Sodafabrikation nach dem Solvayverfahren," pp. 3-4.
⊕. G. R. Robertson, "California Desert Soda," *Ind. Eng. Chem.* 23, 478 (1931).
⊕⊕. G. R. Robertson, "The Trona Enterprise," *ibid.* 21, 520 (1929).
†. U. S. Geol. Surv., Bull. No. 60, pp. 27-101 (1887-1888).
**. Calculated from W. Wallace's Analysis, *Chem. News*, p. 205 (1873).
‡. Chinese Eastern Railway Lab.
§. T. Suzuki.
#. Calculated from I. Obada's analytical results, *Economic Geol.* (Nov., 1930).

pling in extensive deposits (except in the case of soda brine from individual alkaline lakes) also has a bearing on the results. The results of analyses of natural soda samples or of soda brine residues are given in Table 3.

At present natural soda as a whole does not play an important rôle in supplying the world market, and probably it will never do so except in a limited area surrounding the locality where the deposit occurs. With the possible exception of the Magadi and California deposits, the difficulties of transportation have been an unfavorable factor. Then again, because of the low purity of natural soda due to the presence of large amounts of sodium bicarbonate, more or less sodium sulfate, considerable amounts of sodium chloride, and sometimes also borax, and because of the small scale on which it can be operated, it cannot compete with ammonia soda in industries which require a high-grade product. Any attempt at refining it, *e.g.*, by dissolving, settling, recarbonating, and furnacing the product, would involve almost the same cost of manufacture as ammonia soda.

In the case of California deposits, however, the operation has held its own, because of the many valuable by-products obtained. Among those by-products may be mentioned potassium chloride, borax, sodium sulfate, bromine, etc. It was usual to subject the natural product to a simple process of crushing, washing, and drying; but this treatment did not remove the many impurities present. However, a fractional crystallization method has been developed in the plant of the American Potash & Chemical Corp., using Searles Lake underground brine based on the principles of the phase rule, whereby a double salt known as burkeite is obtained, from which now a very pure soda ash is produced. Since 1934, with the improved quality of soda ash produced by this Corporation comparable to ammonia soda ash, natural soda has become a real competitor in the soda market on the Western Coast of the United States.

Diversion of the Owens River in Eastern California to Los Angeles aqueduct in 1917 dried up Owens Lake, to which the river formerly flowed. This lake and the Searles Lake are now the most important sources of natural soda in the United States. Numerous other soda lakes exist on the North American continent, but they are not important sources of supply. The first company for exploiting natural soda was organized by C. F. S. Wrinkle,* with the financial help of D. O. Mills, on Owens Lake in the early 1880's, about the same time as the Solvay process for ammonia soda manufacture was introduced into America. This concern, under the name of the Inyo Development Company, was operating continuously at Keeler until 1920, three years after Owens River was diverted to Los Angeles aqueduct. For many years since 1885, this company concentrated brine from Owens Lake by solar evaporation in huge clay vats, covering acres of ground. These vats (fields) were filled with brine 6-8 inches deep, and the precipitated trona was harvested once a year in the

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* Hirschkind, W., Alkaline Lake Brines Supply Western Soda Products, *Chem. Met. Eng.*, **38**, 657 (1931).

form of crust about $\frac{3}{4}''$ thick. The product was calcined in a reverbera-
tory furnace, but was impure, containing only 95 per cent Na_2CO_3. In
1912, Noah Wrinkle, one of the engineers of the Inyo Development Co.,
established another plant at Keeler on Owens Lake under the name of
Natural Soda Products Co. to exploit the crude soda from the lake. Some
bicarbonate of soda and natural trona were made by this company. The
purity was 97-98 per cent Na_2CO_3. Later, Natural Soda Products Co.
introduced Oliver filters for filtering sodium bicarbonate and rotary dryers
for calcining it to light ash. Recently this company built a new plant
just south of Keeler, having a daily capacity of 100 tons of soda ash.
Much of its output was shipped to Japan and Sweden for some years.

In the Natural Soda Products Co.'s plant at Keeler on Owens Lake,
the brine was concentrated by solar evaporation and enriched by solid
trona. It was carbonated in wooden towers, using CO_2 gas from lime
kilns burning native dolomite. Sodium bicarbonate in the slurry from
the towers was filtered in the usual way and calcined into light ash having
the following composition:

TABLE 4. Composition of Light Ash at Keeler.*

Na_2CO_3	98.16%
$NaHCO_3$	0.90
$Na_2B_4O_7$	0.33
Na_2SO_4	0.33
SiO_2	0.25
$NaCl$	0.05
Fe_2O_3 and Al_2O_3	0.02
$CaCO_3$	trace
$MgCO_3$	trace

* G. R. Robertson, California Desert Soda, *Ind. Eng. Chem.*, 23, 478 (1931).

To make dense ash, the light ash was melted in an oil-fired furnace
and atomized by means of compressed air into an insulated space lined
with a fire-proof material. This gave globules of soda ash which is very
dense and particularly favored by glass manufacturers, although the
process is somewhat antiquated. The presence of borax in the soda ash
is not unwelcome to glass manufacturers. A certain quantity of "water
ash" is also made at this plant by the same method as used by the
ammonia soda manufacturers in the East, and this of course yields a less
dense ash. A combination of the two dense ash products gives several
grades of dense ash, having the bulk densities lying in between.

About 1908, the California Trona Company was organized and estab-
lished on Searles Lake. In 1913, this company was succeeded by the
American Trona Corp. In the summer of 1936, the corporation's name
was again changed to the present American Potash & Chemical Corp. It
is considered to be the largest and the most progressive of its kind.

Before this time F. M. Smith founded the West End Chemical Co. on
the southwest shore of Searles Lake at West End. This company car-
bonates borax brine and precipitates sodium bicarbonate in towers from

the brine. Some borax comes down with the bicarbonate, thus yielding a somewhat lower grade of soda ash, containing borax as one of the impurities. Borax then is recovered by crystallization from the mother liquor after the precipitation and filtration of sodium bicarbonate.

Early in 1917, because of demand for soda ash during the World War I (1914-1918), a group headed by Great Western Electro-Chemical Co. built a natural soda plant on the southwestern shore of Owens Lake. The plant was built at Cartago and was known as the California Alkali Co. This plant built lime kilns and used also wooden towers, rotary vacuum filters and rotary soda dryers, and produced marketable soda ash both in light and dense form. In 1924, this company was merged with Inyo Development Company and became the Inyo Chemical Co. The Keeler Plant of the Inyo Development Company was then leased to Natural Soda Products Co. which operated it more or less steadily. The Cartago plant of the California Alkali Company discontinued operation in 1932.

In 1926, a Los Angeles group built a plant at Bartlett on the west shore of Owens Lake about 10 miles south of Lone Pine under the name of Pacific Alkali Company. This company pumps brine through $2\frac{1}{2}$ miles of 14″ pipes into large open vats which concentrate it by solar evaporation to 12-14 per cent soda. The soda brine is then carbonated and the slurry drawn off and centrifuged. The cake from the centrifuges is calcined in a Herreshoff furnace into soda ash, and is screened and packed for shipment. The mother liquor from the centrifuges is cooled to crystallize out borax and the crude borax crystals are filtered. This filter liquor is returned to the lake. The plant produces about 1000 tons of soda ash and 2000 tons of borax per season.

In 1917, a Denver group under the name of Chemical Products Co., built a caustic soda plant on the northwestern corner of Owens Lake at Bartlett, the equipment for which came from an abandoned caustic soda plant at Green River, Wyoming. The plant was erected but never operated. The property was later bought by a Boston group, who rebuilt the plant and operated it under the name of Clark Chemical Co. But the plant was shut down in 1928 and the company dissolved in 1931.

In 1924, a caustic soda plant was built by Great Western Electro-Chemical Co. at Pittsburg, Calif., to causticize natural soda from Owens Lake. In 1928, the same company built another caustic unit in the plant of the Stauffer Chemical Co. at Los Angeles, Calif.

A natural soda plant, called Sodium Products Co.* exists near a town called Wilson Creek about 100 miles west of Spokane, Wash. The deposit is in a lake occupying about 13 acres, and consists of sodium carbonate mixed with insoluble silt. Water is piped in from nearby springs to leach soda from a pit dug in the deposit, and is heated to about 100° F. by live steam, until the warm water dissolves enough soda to show a Baumé reading of 32°. The solution is then pumped to settlers, filtered, cooled

*Lindsay, J. D., Producing Natural Soda Ash in Washington, *Chem. Met. Eng.*, 45, 144 (1938).

and allowed to crystallize in a series of crystallizing tanks. The crystals are given a preliminary drying by warm air and are then heated to a thick consistency on steel belt conveyers by gas burners. The plastic mass of crystals is then extruded between rubber rolls into granules which are dried to granular ash.

In 1939, the U. S. Geological Survey discovered a large deposit of trona at a depth of from 1300 to 1600 feet in Sweetwater County, Wyo. These trona beds were found in cores of the John Hay Oil and Gas Well drilled by Mountain Fuel Supply Co. The trona is associated with small quantities of northupite $(Na_2CO_3 . NaCl . MgCO_3)$ and pirssonite $(Na_2CO_3 . CaCO_3 . 2H_2O)$ and may form an important source of natural soda in future. J. J. Fahey, Chemist of the U. S. Geological Survey Laboratory, identified in the deposit a new mineral in the form of a double carbonate of sodium and calcium, $(Na_2CO_3 . 2CaCO_3)$ which he named "Shortite" [†] in honor of Dr. Maxwell N. Short, Professor of Optical Mineralogy at the University of Arizona.

Among the larger manufacturers operating natural soda plants therefore may be mentioned the American Potash & Chemical Corp. at Trona; the West End Chemical Co. at West End; the Pacific Alkali Co. at Bartlett; and the Natural Soda Products Co. at Keeler. The first two named are located on Searles Lake, Calif., and the last two on Owens Lake, Calif. Of the four companies mentioned, three are now operating; namely, the American Potash & Chemical Corp., the West End Chemical Co., and the Pacific Alkali Co. The Natural Soda Products Co. is operating intermittently, while the Inyo Chemical Co. at Cartago, on Owens Lake, has been shut down since 1933. This plant was sold to the Great Western Electro-Chemical Company. At the present time, the combined annual production of all the natural soda plants totals well over 100,000 tons of soda ash, being approximately 4 per cent of the total annual production of the ammonia soda plants in the United States. Some of these products are accepted as on a par with the ammonia soda ash as regards purity, notably soda ash from the American Potash & Chemical Corp. at Trona on Searles Lake, as mentioned above.

At Lake Magadi in Kenya Colony in the British East Africa, natural soda was produced by Magadi Soda Co., Ltd., controlled by the Imperial Chemical Industries, Ltd., of England. Export of natural soda from Lake Magadi amounted to 65,137 tons a year in 1929. The deposit was exploited since 1911. Because of the decline of natural soda, the Imperial Chemical Industries, Ltd. (I.C.I.) arranged with the Kenya Government for a moratorium on their contract with the Kenya Government for the annual production of 100,000 tons of natural soda from Lake Magadi. Lake Magadi has probably the largest natural soda deposits in the world, being estimated at about 20 million tons of sodium sesquicarbonate. At present, the soda ash output as reported from the quantities exported from Kenya Colony is as follows:

[†] Fahey, J. J., Shortite, A New Carbonate of Sodium and Calcium, *American Mineralogist*, 24, 514 (1939).

TABLE 5. Sodium Carbonate Exported from Kenya Colony.*

Year	Long Tons
1929	65,137
1930	49,270
1931	44,171
1932	37,263
1933	43,051
1934	30,832
1935	38,723
1936	46,549
1937	41,330
1938 (8 months)	33,637
1939	40,983

* "The Mineral Industry," 1939; 1940.

Lake Magadi could be worked to produce 100,000 tons of soda ash annually, but the market could take only about 50,000 tons. Formerly, much of the soda was sold to Japan. From about 1937, export from Magadi has again declined because of the increased production of ammonia soda ash in Japan. The outlook for the future of the Magadi soda export is not very bright, because both Australia and India have built their own ammonia soda plants.

In Egypt, natural soda is worked by the Egyptian Salt and Soda Co., Ltd., mainly for caustic soda, the total output being a little over 3000 tons of caustic soda yearly.

In South Africa at Hamans Kraal near Pretoria, there is a small natural soda plant producing about 3000 tons yearly. The raw materials are soda brine and trona.

In India, a small quantity of crude natural soda "Chanio" is recovered by the Sind, the total production being less than 1000 tons per year.

In China, a great deal of natural soda was obtained from soda lakes ("Nor") in the Four Eastern provinces and in the provinces of Inner Mongolia. As a rule, it was made into blocks (see Soda Blocks, Chapter XVI) for convenience of transportation. Before any ammonia soda ash was imported or manufactured in the country, as much as 200,000 tons of natural soda were supplied from this source yearly.

In Canada, there has been only a small production from the Canadian deposits. The figures are as follows:

TABLE 6. Production of Canadian Natural Soda.

Year	Tons	Year	Tons
1928	519	1935	242
1929	600	1936	192
1930	364	1937	286
1931	712	1938	252
1932	495	1939	300
1933	559	1940	220
1934	244		

Data on natural soda deposits are scattered and very incomplete. Many plants are unreported, but they are small and not of importance. Some of them operated for a short time and stopped. Many of these

have passed through vicissitudes of fortune, and have suspended operation. It is likely, however, that large natural soda producers like American Potash & Chemical Corp. will remain a potential competitor of the ammonia soda manufacturers in the adjoining territories.

Statistics of the production of natural soda in the United States for the period between 1921-1939 inclusive are given in Table 7.

TABLE 7. Production of Natural Soda in the United States.*

Year	Short Tons	Year	Short Ton
1921	17,000	1931	78,530
1922	33,537	1932	55,377
1923	35,440	1933	70,461
1924	44,890	1934	88,325
1925	45.910	1935	93,230
1926	56,750	1936	102,866
1927	67,240	1937	104,711
1928	79,830	1938	100,010
1929	102.930	1939	124.743
1930	90,300	1940	130,034

* "Mineral Industry" (1931), p. 502; "Minerals Yearbook" (1940).
The figures given above include soda ash, sodium bicarbonate and sesquicarbonate; the 1930-1931 figures also included sal soda.

Table 8 is a partial list of some natural soda compounds and their crystalline forms.

TABLE 8. Some Natural Soda Compounds and Their Crystalline Forms.

Descriptive Name	Mineralogical Name	Formula	Form Crystalline
1. Decahydrate of soda	Natron	$Na_2CO_3 . 10H_2O$	Monoclinic
2. Monohydrate of soda	Thermonatrite	$Na_2CO_3 . H_2O$	Orthorhombic
3. Sesquicarbonate of soda	Trona or Urao	$Na_2CO_3 . NaHCO_3 . 2H_2O$	Monoclinic
4. Sodium-calcium carbonate penta-hydrate	Gaylussite	$Na_2CO_3 . CaCO_3 . 5H_2O$	Monoclinic
5. Sodium-calcium carbonate dihydrate	Pirssonite *	$Na_2CO_3 . CaCO_3 . 2H_2O$	Orthorhombic
6. Sodium carbonate-chloride and magnesium carbonate	Northupite *	$Na_2CO_3 . NaCl . MgCO_3$	Octahedral
7. Sodium-magnesium carbonate and sodium sulfate	Tychite *	$2Na_2CO_3 . 2MgCO_3 . Na_2SO_4$	Octahedral
8. Sodium carbonate-sulfate and potassium chloride	Hanksite *	$2Na_2CO_3 . 9Na_2SO_4 . KCl$	Hexagonal
9. Sodium-aluminum carbonate and aluminum hydroxide	Dawsonite	$Na_3Al(CO_3)_3 . 2Al(OH)_3$	Monoclinic(?)
10. Sodium carbonate-sulfate	Burkeite †	$Na_2CO_3 . 2Na_2SO_4$	Monoclinic(?)
11. Sodium-calcium carbonate	Shortite ‡	$Na_2CO_3 . 2CaCO_3$	Orthorhombic

* Occur in Searles Lake deposits.
† J. E. Teeple, "The American Potash Industry and Its Problems," *Ind. Eng. Chem.*, Mar. 1929. "The Industrial Development of Searles Lake Brines," John E. Teeple, New York, Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1929.
‡ Fahey, J. J., *American Mineralogist*, 24, 514 (1939).

AMERICAN NATURAL SODA PROCESSES TODAY

As mentioned above, only three companies are at present operating the natural soda plants on the West Coast in the United States, namely the American Potash & Chemical Corporation at Trona on Searles Lake; the West End Chemical Co. at West End, also on Searles Lake; and the

FIG. 4. Natural soda plants in California.

1. Natural Soda Products Co.,
   Keeler, Owens Lake.
2. Pacific Alkali Co.,
   Bartlett, Owens Lake.
3. Inyo Chemical Co. (California Alkali Co.),
   Cartago, Owens Lake.

American Potash and Chemical Corp.,
Trona, Searles Lake.
West End Chemical Co.,
West End, Searles Lake.

Pacific Alkali Co. at Bartlett on Owens Lake. The Natural Soda Products Co. at Keeler on Owens Lake, in which Michigan Alkali Co. was interested, suspended operation in about 1937 on account of dilution of brine due to flood conditions. The older companies, such as Inyo Chemical Co., which was sold to the Great Western Electro-Chemical Company in 1931, the Boro-Solvay, started by the Solvay Process Co. and sold to

the American Potash & Chemical Corp., etc., have ceased to exist. Figure 4 shows the location of these plants.

Of the three companies now actually operating, the American Potash & Chemical Corp. is the largest and has the most complete line of products, working on processes based on scientific control and physicochemical principles. The American Potash & Chemical Corp. alone produces 500 tons of KCl, 280 tons of borax, 250 tons of Na_2SO_4 and 140 tons of soda ash per day, besides certain quantities of liquid bromine and dilithium sodium phosphate. This Corporation produces soda ash directly in a dense form, and the West End Chemical Co. and the Pacific Alkali Co. both produce light ash as the initial product.

The Pacific Alkali Co. at Bartlett on Owens Lake carbonates its brine by means of flue gases from an oil-fired furnace containing about 14 per cent CO_2. At this plant, soda in the brine is partially carbonated to the sesquicarbonate stage in 6' dia. × 80' high towers and the sodium sesquicarbonate crystals are filtered off from the liquor. The filter liquor is then cooled to produce crude borax crystals. Sodium sesquicarbonate is dried at a low temperature using steam-heated air dryers, or is calcined to soda ash in a furnace of the Herreshoff type.

The West End Chemical Co. at West End on Searles Lake carbonates the brine with lime kiln gas as in the ammonia soda practice, except that wooden carbonating towers are used. Soda in the brine is carbonated to sodium bicarbonate, which is filtered off from the slurry by means of rotary vacuum filters. The filter liquor is chilled to obtain crude borax crystals, but only a portion of the total available borax is recovered this way. The bicarbonate is calcined to light ash in a rotary dryer in the usual manner. The borax (sodium tetraborate decahydrate) is dried on steam-heated air dryers. Some borax comes down with sodium bicarbonate in the towers, and so the soda ash made is not of the highest quality.

The process used in the American Potash & Chemical Corp. is a complicated and most scientific one, based on the study of phase-rule solubility diagrams made by Dr. John E. Teeple and his co-workers and put into execution successfully by Mr. R. W. Mumford and his assistants. The company was originally organized under the name of the American Trona Corporation in 1913, and the plant started small production in 1914. Up to 1919 only potassium chloride was produced. From 1919 on, borax was added as another product. In 1926 the name was changed to the American Potash & Chemical Corporation, and thereafter production rapidly increased. Here the brine is pumped by vertical turbine-type centrifugal pumps from some 20 8"-bore wells sunk to between 90 and 100 feet below the surface. The brine * contains, besides small quantities of other salts,

NaCl	16.35%
NaSO₄	6.96%
KCl	4.70%
Na₂CO₃	4.70%
Na₂B₄O₇ . 10H₂O	2.84%

* Gale, W. A., "Chemistry of the Trona Process," *Ind. Eng. Chem.*, **30**, 869 (1938).

and has a pII value of 9.48. It has only traces of calcium and magnesium, and contains a little tungstate, bromide, and lithium salt. As the processes are based on phase-rule studies, and are both interesting and instructive, we shall describe them in considerable detail.

The brine is sent by a horizontal centrifugal booster pump into the plant in 12″ steel pipes, some four miles long, and the whole pipe line is lagged with hair and asbestos paper to prevent excessive heating by the desert sun. The raw brine is clear and has a specific gravity of 1.3. It is first used as a cooling medium in the condensers of potassium chloride vacuum crystallizers and for washing various filter cakes. It is thus preheated before it is sent into huge triple-effect Manistee evaporators (22 feet diameter by about 40 feet high). These evaporators have 4 outside heaters located at four quadrants and heated by 31 lbs. pressure (gauge) exhaust steam from non-condensing turbo-generators. The brine in the evaporators has a strong tendency to foam, and small drops of coconut oil are introduced to the liquor surface to minimize foaming. The feed to the evaporators is introduced at the third effect and consists of raw brine and a small stream of end liquors in the ratio approximately of 3 parts of raw brine to 1 part of the end liquor. The brine in each effect is circulated by a vertical turbine pump and the slurry is bled to salt traps for the separation of salt (NaCl), burkeite ($2Na_2SO_4 . Na_2CO_3$) and Li_2NaPO_4 crystals. There are two salt traps in series. Salt crystals, being coarser, are separated from the slimy crystals of burkeite and dilithium sodium phosphate, by countercurrent flotation in the first set of salt traps; while the finer burkeite and phosphate crystals settle in the second salt trap and in the Dorr classifier, thus affording a rough separation of these crystals. The crystals are filtered off separately on rotary vacuum drum filters. Salt crystals containing about 97 per cent NaCl are produced at the rate of some 2,000 tons daily and are sent to waste, only a small quantity of the salt being utilized in the process for the separation of burkeite crystals and for cooling in the Glauber salt crystallizer condenser. Burkeite and a small quantity of lithium phosphate are worked up in the process as secondary products.

Operation of these triple-effect evaporators aims by a close chemical control to reach a point just below the saturation point of potassium chloride at a temperature of 235° F. in the first effect of the evaporator, a counter-current feed being used in these evaporators to maintain the highest temperature for the most concentrated liquor in the first effect in order to prevent precipitation of KCl. The concentrated mother liquor from the filters and from the overflow of Dorr-classifier (mother liquor No. 1) is then cooled to 100° F. in three-stage vacuum crystallizers with enough dilution water to keep salt in solution, and the crude KCl crystals are filtered on the centrifuges. The filter liquor (mother liquor No. 2) is then cooled by ammonia refrigeration to 75° F., with sufficient condensate returned to the liquor to prevent precipitation of KCl, and seeded for crystallization, when borax crystals (sodium tetraborate decahydrate) are separated in a thickener and the underflow slurry is filtered, yielding

crude borax. The filter liquor and the overflow from the thickener are returned to the evaporators as the end liquor (mother liquor No. 2) together with the raw brine, as mentioned above.

Both the crude KCl and borax crystals are refined. Chemical grade KCl is obtained by redissolving the crude KCl crystals, chlorinating the solution to liberate bromine as a by-product, and recrystallizing to eliminate most of NaCl and NaSO$_4$ impurities. The crude borax crystals are recrystallized by controlled cooling in vacuum crystallizers, and the mother liquor (mother liquor No. 3) is added to mother liquor No. 1 for working up the crude borax. By carefully heating the crystals to incipient fusion in a circular vertical furnace using oil firing, a porous crystalline anhydrous borax is obtained, which is sold under the name "Pyrobor." This is a porous crystalline variety of fused borax, but has not the structure of flinty borax glass which is difficult to grind and to dissolve. The borax crystals are also treated with commercial sulfuric acid, giving boric acid crystals which are then recrystallized as the chemically pure or U.S.P. boric acid and dried in a steam-heated rotary dryer. The fine slippery powder is used in making talcum powder and for medicinal uses.

Since 1934 the plant has also produced soda ash and anhydrous sodium sulfate from burkeite crystals. The burkeite crystals in the slurry from the evaporators are filtered and re-dissolved and the sparingly soluble dilithium sodium phosphate is separated as the residue, which is now the chief source of lithium salts. The solution is warmed to about 28° C. and concentrated in vacuum crystallizers, yielding Glauber salt ($Na_2SO_4 . 10H_2O$) containing a small amount of sodium carbonate monohydrate ($Na_2CO_3 . H_2O$). This Glauber salt is filtered off. To the filter liquor (mother liquor) is added salt (NaCl), which by common-ion effect displaces burkeite from the solution upon warming to a temperature of about 53° C., burkeite being more insoluble at the higher temperature. The burkeite crystals are then filtered off and added to the bulk of burkeite from evaporator slurry for processing. Filter liquor from the burkeite is cooled down by ammonia refrigeration to around 5° C., when sal soda together with a small amount of Na_2SO_4 and NaCl crystallizes out. The sal soda is filtered off and melted in its own water of crystallization. The solution is then evaporated when sodium carbonate monohydrate separates out, leaving most of the Na_2SO_4 and NaCl in solution. The monohydrate crystals are filtered off and dried in an oil-fired rotary dryer to dense ash directly. This dense ash has an apparent density of about 60 lbs. per cu. ft. and has a purity of 99.50-99.75 per cent Na_2CO_3, 0.3 per cent NaCl, and less than 0.003 per cent Fe_2O_3. The mother liquor from the sal soda crystallization containing mainly sodium sulfate and salt is discarded to waste. This grade of soda ash compares very favorably with the highest grade of ammonia soda ash.

Certain users require a bulky ash for their standard packing and therefore object to this dense ash. Light ash is now produced in the works by wetting the dense ash with sufficient water to correspond roughly

to the hydration of sodium carbonate heptahydrate in a rotary cylinder, yielding a granular form of porous mass, which is then dried very slowly in a steam-heated tunnel dryer. The dried mass is then pulverized to about 80 mesh in an impact crusher, and packed as light ash. In this way, it is possible to reduce the bulk density of soda ash to 23 lb. per cu. ft. By varying the ratio of water added, or the rate of drying of the granular mass in the hot-air dryer, or grinding the dried ash to different degrees of fineness, it is possible to effect any degree of lightness. This process achieves the reverse of what a smaller amount of water does to the ammonia soda ash in a somewhat different manner.

For certain crops, such as tobacco and pineapple, and for fruit trees, such as orange and lemon, potassium chloride is not generally used as fertilizer, but potassium sulfate is preferred by the farmers and fruit growers for such purposes. Potassium sulfate is made in the plant by a double decomposition between KCl and burkeite $Na_2CO_3 . 2Na_2SO_4$ when K_2SO_4 is separated by fractional crystallization.

To help the reader to follow this "Trona Process," a schematic diagram of it is given in Fig. 5. No attempt is made to cover all details of modifications frequently made in the plant operation.

The Trona processes [*] are interesting because the brine represents at least a nine-component system which is more complex than the Stassfurt salt deposits in Germany, which may be considered as a five-component system. If the brine were subject to an isothermal evaporation at a low temperature, such as by solar evaporation, then salt (NaCl), glasserite [$K_3Na(SO_4)_2$], sodium carbonate heptahydrate ($Na_2CO_3 . 7H_2O$) and finally potassium chloride would be precipitated more or less together, so that no separation of potassium salts from sodium salts would be possible. However, when evaporation is carried out at a temperature above 100° C., as in multiple-effect vacuum evaporators, only salt (NaCl), burkeite ($Na_2CO_3 . 2Na_2SO_4$) and possibly a small amount of sodium carbonate monohydrate ($Na_2CO_3 . H_2O$) will separate out; while at 113° C. (235° F.) as the liquor is further concentrated and the temperature rises, it is possible to keep all KCl in solution.[†] Consequently, after the salt, burkeite, etc. have been filtered off, and the liquor is cooled from 235 to 100° F., potassium chloride then crystallizes out; but because of the great tendency toward supersaturation on the part of borax crystals, borax remains in solution and only KCl separates. After KCl crystals have been filtered and the liquor further cooled strongly by liquid ammonia, then and only then does borax crystallize out.

Another interesting feature is the separation of sodium carbonate from sodium sulfate in the burkeite. When salt (NaCl) has been roughly separated from burkeite in salt traps and when the burkeite crystals are re-dissolved, Glauber salt by vacuum crystallization in the absence of excess salt separates out from the solution upon cooling. Glauber salt crystals

* Gale, W. A., "Chemistry of Trona Process," *Ind. Eng. Chem.*, **30**, 867 (1938).
† Mumford, R. W., "Potassium Chloride from the Brine of Searles Lake," *Ind. Eng. Chem.*, **30**, 872 (1938).
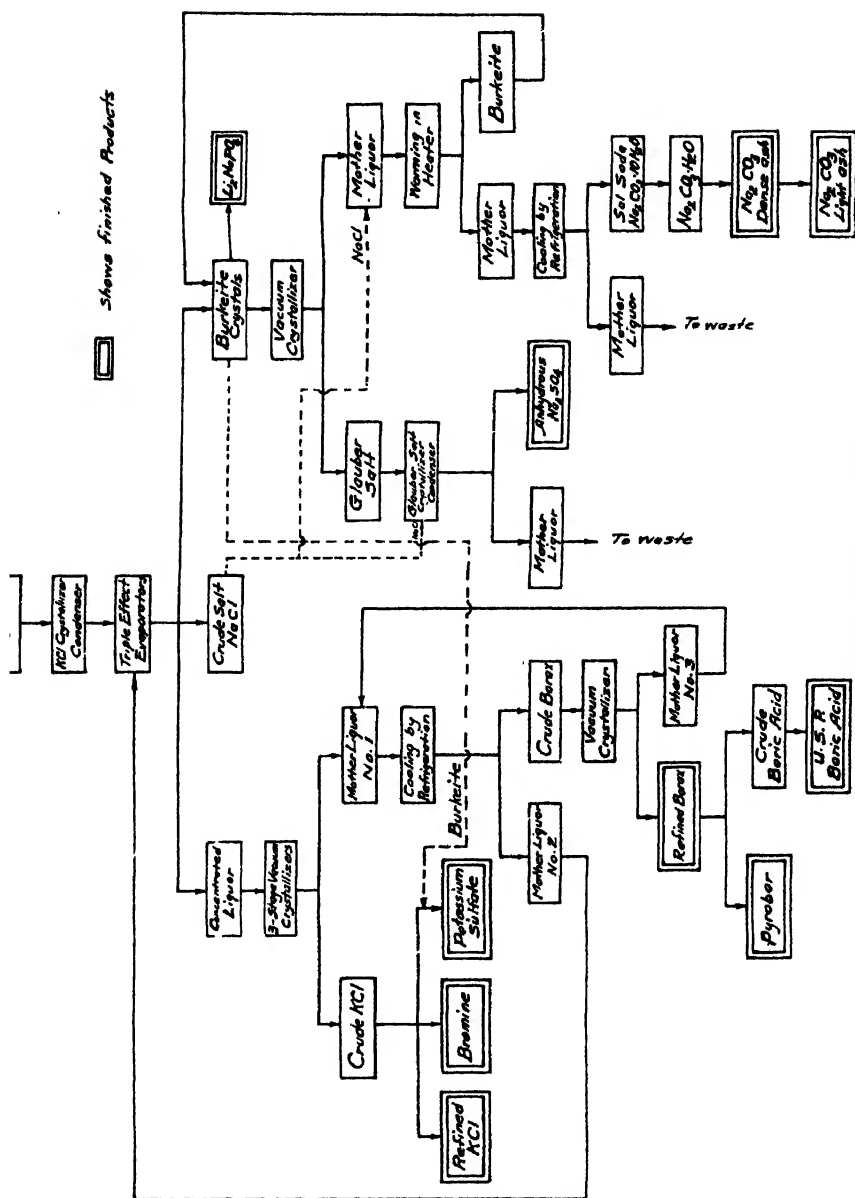
Fig. 5. Diagram of Trona process.

are then filtered off. When, to the mother liquor, an excess NaCl (about 2 per cent) is added, the remaining burkeite separates out as such, leaving sodium carbonate in the mother liquor. By cooling further with ammonia refrigeration, soda then separates out as sal soda ($Na_2CO_3 . 10H_2O$) which necessarily contains some sodium chloride and sodium sulfate as impurities. Recrystallization from sal soda to obtain sodium carbonate monohydrate at a higher temperature eliminates most of these impurities and the monohydrate so obtained yields a very high-grade dense ash upon calcining.

Here the use of NaCl to depress the solubility product of burkeite for the removal of excess burkeite from the Glauber salt mother liquor before crystallization of sal soda is very instructive; while the addition of NaCl to the Glauber salt solution to lower its temperature for use as the cooling medium in the condenser of the Glauber salt vacuum crystallizer, thereby raising the temperature of the Glauber salt solution for the recrystallization of the anhydrous sodium sulfate therefrom, is indeed ingenious (see schematic diagram, Fig. 5).

The conversion of dense ash to light ash represents an interesting manipulation in that it accomplishes the opposite results to the manufacture of "water ash" in the ordinary ammonia soda process, although the details in the application are somewhat different.

An electrolytic plant using potassium chloride for chlorine and caustic potash may be advantageously added in this Trona plant to utilize the excess power and to produce chlorine needed in the bromine recovery, etc. Caustic potash then is again a valuable joint product.

Chapter III
History of Ammonia Soda Process: Statistics

As early as 1811, a Frenchman, L. Fresnel, conceived the idea of making soda from salt and ammonium carbonate. A German, A. Vogel, claimed that his father discovered in 1822 the reaction between ammonium carbonate and brine, whereby sodium bicarbonate was produced. In 1837, an English chemist, John Thom, attempted to make soda, using the reaction between ammonium carbonate and salt. He succeeded in manufacturing some 200 kg. of soda from this reaction. In the year 1838, H. G. Dyar and J. Hemming patented in England the treatment of brine with ammonium bicarbonate to precipitate sodium bicarbonate, outlining the process with considerable detail and accuracy. Dyar and Hemming erected a plant at Whitechapel, London, but it was not a financial success. In 1839, Delaunay patented the process in France on behalf of Dyar and Hemming. A. A. Canning in 1842 patented the process of carbonation with gaseous carbon dioxide, and in 1852 Crinus in France attempted to recover carbon dioxide gas from the calcination of sodium bicarbonate. In the same year, W. Chisholm patented the process for the recovery of ammonia from the mother liquor by the distillation of the liquor with lime and the subsequent absorption of the ammonia in brine. Thus, as early as 1852, all the main reactions in the ammonia soda process—the formation of sodium bicarbonate, the calcination of the bicarbonate with recovery of carbon dioxide gas, the recovery of ammonia by distillation with lime and absorption of the ammonia gas in brine—all were definitely known. In 1854, T. Schloesing patented the same process in France and in 1855 built a factory at Puteaux near Paris for its exploitation. By 1858 Schloesing and Rolland had patented the complete process in France again.

Plant after plant attempting to use the process then failed. The works erected by James Muspratt, the founder of the LeBlanc soda industry in England, at Newton, Lancashire, in about 1840 and that erected by William Gossage and Henry Deacon at Widnes, Lancashire, in 1853, both were in operation for two years but could not compete with the LeBlanc process. Deacon then erected a LeBlanc soda works instead. The works erected by Schloesing and Rolland at Puteaux, promising for a time a good prospect of success, lasted also for about two years. By 1860, nobody seemed to be able to make the process a success commercially.

In 1861, Ernest Solvay, a Belgian, independently discovered the same process and in 1863 a company called Solvay et Cie was organized in Brussels to manufacture soda, with a capital of 136,000 fr. A plant was erected at Couillet, Belgium, and operation started in 1865. Ernest Sol-

vay and his brother Alfred devoted their whole life and energy to the improvement of the apparatus. In the year 1866, that plant produced 1½ tons of soda ash per day and in 1867 the product was shown in the Paris exhibit. In 1869 the plant was doubled and the production trebled. By 1872 Solvay was able to produce 10 tons of soda per day. In the same year (1872) Solvay designed a large plant erected at Dombasle near Nancy, France.

In 1872, Ludwig Mond in England had an understanding with Solvay and the outcome was that in 1874 a plant was erected at Winnington near Northwich, Cheshire. This marked the beginning of the ammonia soda process in England and the firm of Brunner, Mond & Co., Ltd. (founded by John Brunner and Ludwig Mond) was then formed. This was also the first company to use natural brine for the manufacture of soda. This company now has a plant at Winnington, near Northwich, one at Sandbach, one at Lostock Gralam, one at Middlewich, and a new plant at Wallerscote, all in Cheshire. The principal works are in Winnington, Lostock Gralam, and Sandbach with a new works at Wallerscote for future expansion. The total output from these plants amounts to over 3,500 tons per day, with a maximum daily capacity of more than 4,000 tons.

Besides France and England, Solvay also built plants in Germany, Russia and other principal countries in Europe, as well as in the United States. Solvay brothers had an interest in all these plants and these were more or less closely connected. It was thus a huge international syndicate having its headquarters in Brussels, Belgium. It was through the organizing ability and personality of Ernest Solvay (Fig. 6) that it was possible to manage such a huge international institution, forming a connecting link between some twenty-six of such member plants throughout the world. Ernest Solvay also arranged for an interchange of technical information and operating data among these member plants. Such operating data and results were compiled and circulated monthly among all member plants, so that the technical staff of one plant had access to all such data and had before it the best set of operating results obtainable concerning any one step of the process in any one of the individual plants during the current month.* It was possible also to arrange for an operating engineer from one plant to visit any one of the other plants to observe certain improvements and study features peculiar to that particular plant with a view to improving equipment by the experience of the other plants. The center of these interests was in Brussels. There an International Committee consisting of technical experts and operators from each country sat yearly to discuss technical improvements and problems concerning operation, or to compare notes and discuss progress made in the other parts of the world.

In America, the ammonia soda industry was started by William B. Cogswell, who went to Belgium to negotiate with Ernest Solvay for the

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*Trump, Edward N., "Looking Back at 50 Years in Ammonia Soda," *Chem. Met. Eng.*, **40**, No. 3, 126 (1933).
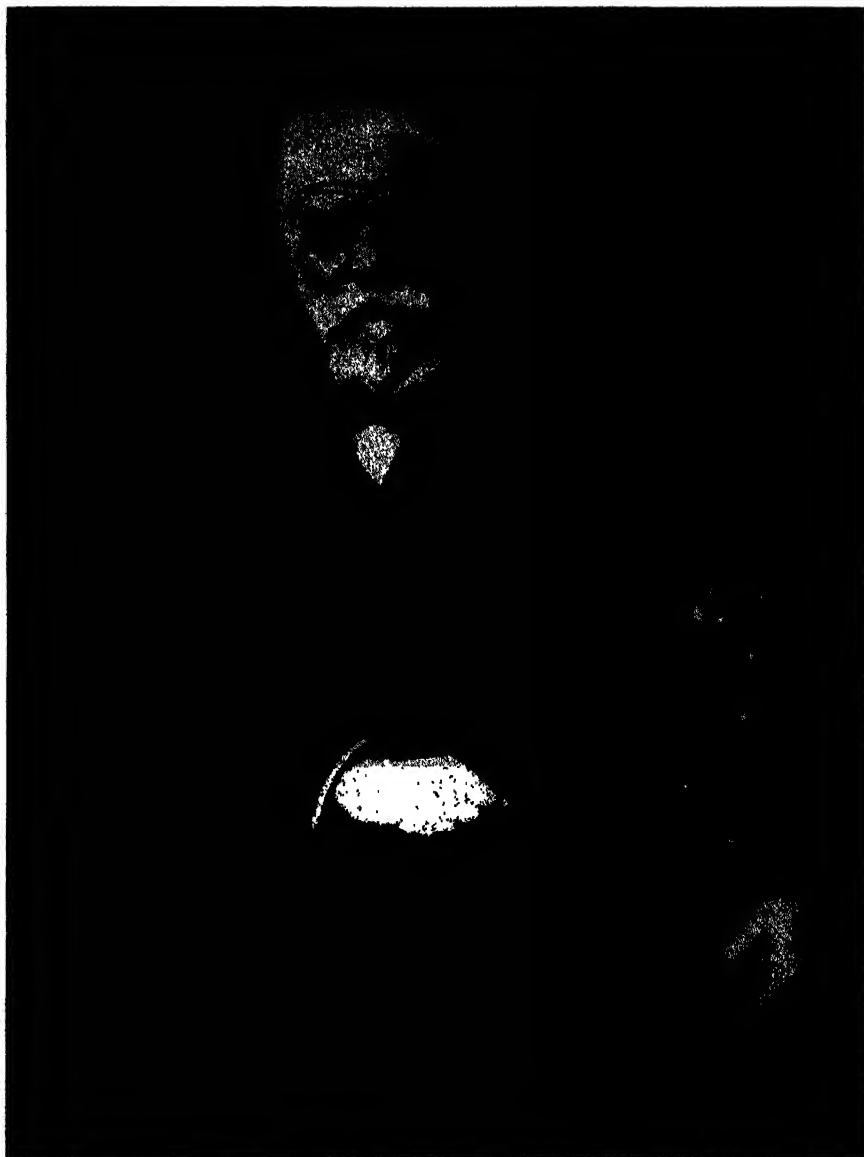
Fig. 6. Ernest Solvay (1836-1922)

use of his process. For this purpose the Solvay Process Co. of Syracuse, N. Y., was organized in 1881 with Rowland Hazard, of Providence, R. I., a mine owner, as President; William B. Cogswell as Manager and Chief Engineer, and O. V. Tracey as Secretary and Treasurer. During the construction period, Cogswell brought William L. Neill, a chemist, and later also Henry Cooper and Nicholas Bodot, to the Dombasle Works of

Solvay and Co. to study the process. The plant at Syracuse was completed in January, 1884, when operation was started. Although the process had been proved successful, operation at Syracuse was attended with
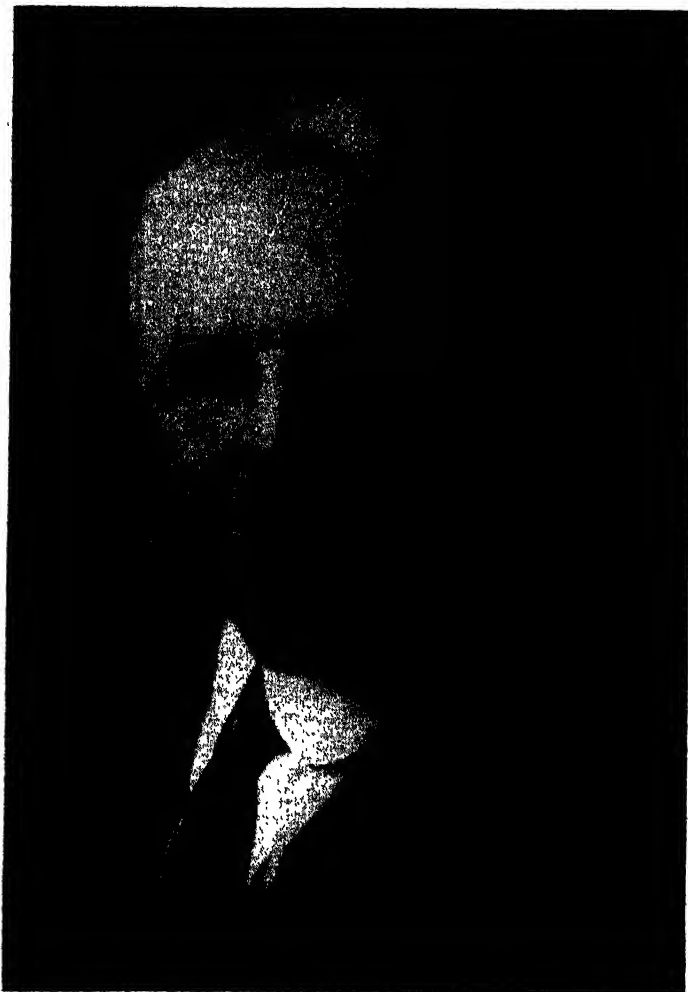
Fig. 7. Edward Needles Trump (1857-....).
A pioneer and veteran of the American Alkali Industry.

many difficulties. Only three of the employees in the whole plant had been to an ammonia soda plant, and none had ever operated one or had had any experience with it. Problems arose daily, but through the skill of Mr. Cogswell assisted by his assistants, among whom was Mr. Edward N. Trump, the output of the plant was tripled in 1887 and increased tenfold ten years later (Fig. 7).

In 1879, a paper entitled "The Manufacture of Soda by the Ammonia Process" was presented by Oswald J. Heinrich to the Baltimore Meeting of the American Institute of Mining & Metallurgical Engineers, giving an interesting account of the comparative status between the LeBlanc process and the ammonia soda process at that time, still not entertaining much hope for the latter. Meanwhile, Herman Frasch, of sulfur fame, had built and attempted to operate a small plant at Bay City, Mich.; but the operation was not successful, and the plant finally had to be dismantled.

The Solvay Process plant at Syracuse was so successful that in 1898 another plant was built at Delray, Mich. The Syracuse plant today is the largest in the country and also the largest single ammonia soda plant in the world. During the first World War (1914-1918), the Kansas Chemical Company's plant at Hutchinson, Kansas, was leased, remodelled and later bought by the Solvay Process Co.; but immediately after the war the plant was shut down, because operation was found to be uneconomical because of small capacity and distance from a limestone supply.

In 1917, Solvay Process Co. of Syracuse, in conjunction with the then Brunner, Mond & Co., of England (now Imperial Chemical Industries, Ltd.), built a plant of about 150-ton capacity at Amherstburg, Ontario, near the mouth of the Detroit River in Canada. The plant was designed and built by Mr. Trump and his engineers at Syracuse and operated by them. The plant was under the name of Brunner-Mond (Canada), Ltd., of which Mr. Trump was concurrently president. Later, the plant was bought over and completely owned by the Solvay Process Co. of Syracuse, although the name has remained Brunner-Mond (Canada), Ltd. This plant was designed with due regard to future extension and is well situated as regards the supply of raw materials, limestone being quarried on the plant site and brine wells located only a few miles away.

Among the independent plants, there are several in the United States. These are: Michigan Alkali Co., Wyandotte, Mich.; Diamond Alkali Co., Fairport, O.; Columbia Alkali Corp., Barberton, O.; and Mathieson Alkali Works, Inc., Saltville, Va. Solvay Process Co. is now in reality also an independent company. Ever since the merger into Allied Chemical & Dye Corp. in 1920, and especially after 1925, it broke all ties with the European Solvay interests, although about 20 per cent of its stock is still held by the Solvay group across the Atlantic. In addition there are three or four natural soda plants in California east of the Sierras. (See Chapter II, Natural Soda.)

In England, there was an independent soda plant at Fleetwood, owned by United Alkali Co., Ltd., but this company is now a part of Imperial Chemical Industries, Ltd. (I.C.I., Ltd.), of which Brunner, Mond & Co., Ltd. is a controlling member. The latter also controlled Magadi soda deposits in Kenya Colony, East Africa. (See Chapter II, Natural Soda.)

In the United States, the ammonia soda industry is definitely tending to migrate southward to the Gulf Coast. Of those who have located soda plants in the South may be mentioned Columbia Alkali Corp., Mathieson

Alkali Works, Inc., and Solvay Process Co. (Allied Chemical & Dye Corp.). The plant of the Columbia Alkali Corp. is located at Corpus Christi, Texas, and is known as Southern Alkali Corp. It was designed and built by engineers of the Columbia Alkali Corp. at Barberton, and is partly owned by the Pittsburgh Plate Glass Co. and by the American Cyanamid Co. Because of the business depression in the United States, construction was not started until late in 1933, although the plan had been under consideration for over three years prior to that time. The first unit of 250-ton capacity of soda ash per day was completed and its operation started in October, 1934. Another unit is now installed, so that the total capacity will be about 450 tons per day.

The Mathieson Alkali Works' plant is located at Lake Charles, La. Construction was started at the end of 1933 and was completed in the beginning of 1935. The plant has about the same capacity (450 tons per day), although at the start of the initial operation some trouble was experienced in burning the oyster shells. The design was made by Mr. Edward N. Trump assisted by younger engineers.

Solvay Process Co. entered the field somewhat later and located its plant at Baton Rouge, La. After rapid construction, the Solvay plant was completed and put into operation in June, 1935. This plant is somewhat larger than the other two. It also does not depend upon the shell deposits for limestone supply.

All three plants use rock salt from salt domes by simple brine-well methods. The Mathieson Alkali plant depends entirely on oyster shells for its supply of limestone. Besides, it has a synthetic "sulfate" of soda plant which makes soda ash-sulfur sinter by sintering soda ash and elemental sulfur in molecular proportions. All three plants have caustic soda plants attached, and two of them also have electrolytic caustic plants. These plants differ from the older, inland plants only in certain refinements in the apparatus. The Solvay Process plant is unique in that there is no boiler or turbine plant, since both steam and electric power are advantageously purchased from the adjacent Louisiana Steam Products Corp., which supplies power to the mammoth refinery owned by the Standard Oil Co. of Louisiana at Baton Rouge. The Mathieson Alkali Plant at Lake Charles is probably unique in that the entire compression of CO_2 gases into carbonating towers, or columns, is accomplished by means of centrifugal turbo-compressors instead of piston type CO_2 compressors. The plant also burns oyster shells for lime exclusively. The Southern Alkali plant is unique in that the calcination of ammonia soda to soda ash is done in high-pressure, steam-heated equipment rather than in direct-fired rotary dryers. The plant possesses an abundant supply of petroleum and natural gas, and uses mostly oyster shells for its limestone supply.

The three southern alkali manufacturers were all led to locate alkali production on tidewater by the economic advantage of delivering to their customers by sea route rather than by rail. Up to 1933, all alkali produced by the ammonia soda process in the United States came from

inland plants. With the outstanding development of artificial sodium nitrate for fertilizer from soda ash, and the tremendous tonnage thereof manufactured and shipped to foreign countries from Hopewell, Va., the industry began to appreciate that a large part of the cost of soda ash at the consumer's plant was in the freight. The Hopewell nitrate plant converts soda ash to sodium nitrate with the nitric acid from the oxidation of the synthetic ammonia.* Consumption of soda ash by this one plant alone is equal to the capacity of a fairly large ammonia soda plant. The ash was shipped from Syracuse in canal barges and ocean vessels during a relatively short shipping season over the New York State barge canal.

Investigation as to the possibility of locating alkali plants on the Gulf Coast was made a number of years ago. Besides good shipping facilities on the Gulf Coast, there were many other considerations. An increased demand, especially for caustic soda, has existed in the Southern States because of the growing petroleum, rayon, and cotton industries. Abundance of raw materials for soda manufacture is in evidence. Vast salt domes are found which contain very high-grade salt. Oyster shell deposits, which may be burned to make a good grade of lime, are found in abundance along the beach. Fuel in the form of natural gas or oil is plentiful and cheap everywhere in the region. These naturally provide an ideal location for an ammonia soda industry. All these, coupled with location on tidewater for shipping to coastal states on the Atlantic Seaboard, give these plants a decided economic advantage over the older, inland plants. It is estimated that, given a good capacity production, the cost of manufacture will be as low as $5.50-$6.00 per ton of soda ash (not including freight or sales expenses).

Recently new ammonia soda plants have been added to certain countries, such as Japan, China, Australia, India, etc. In Japan, since the remodeling of the Asahi Soda Co.'s plant by the late Mr. Harald Ahlqvist in 1934, the output of that plant has been almost tripled. New plants have also been added: one in Darien, a regular Solvay process plant; one in Konan, Korea, with a capacity of 100 tons a day designed by Zahn & Co. of Berlin, Germany; and another a small Zahn plant located in Japan proper. In West China, a new plant is under construction. In Australia, a new plant has been completed at Port Adelaide, and was placed in operation in 1940 by Imperial Chemical Industries, Ltd. The plant has about 100 tons of soda ash daily capacity and cost over £1,000,000 for its construction. Salt is obtained from sea water, and limestone is available near the factory. In India, two new plants are under construction: one at Khewra, Punjab, by Imperial Chemical Industries, Ltd., and the other at Mithapur, Kathiawad, by Tata Chemicals, Ltd. True, most of these new plants are small, but they will surely form starting nuclei and grow as the technique of operation is mastered by the plant operatives.

Considerable work has been done on the ammonia soda process, but

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* Within recent years, there has been perfected a process for converting salt directly to sodium nitrate with the nitric acid in this plant, chlorine being formed as a joint product.

what has been published deals mainly with the theoretical side of the subject, mostly from the application of the phase rule and mass action principles. Among the classical investigators of this field may be noted such names as Fedotieff, Jaenecke, etc. Since 1872, a great mass of work has been done to improve the mechanical operation of the process, although little has been added to the public knowledge. A large number of patents has also been taken out mostly on the invention or the improvement of equipment, but this does not mean that such equipment was all in use or stood the test of practice. Many modifications have been proposed regarding the method of working up the mother liquor for ammonium chloride.

Recently some fundamental research work on the ammonia soda process was done by several Russian chemists, and the results were published and made available to the public. In the United States, similar research was made somewhat later by the Mathieson Alkali Works, Inc. at Saltville, and the results checked quite closely with the published Russian figures.

<div align="center">STATISTICS</div>

After the plant was established by the Solvay brothers, the annual production between 1864 and 1868 was 300 tons per year. By 1916, the total world output by this process was 3,000,000 tons, while in the same year the United States alone produced over a million tons of soda ash (all by the ammonia soda process), not including products in other forms.

TABLE 9. Earlier Production of Soda Ash in the United States (in short tons).*

Year	Tons	Year	Tons
1900	362,806	1914	980,224
1904	600,008	1915	1,175,962
1909	740,455	1916	1,194,183
1910	770,978	1917	1,390,625
1911	854,370	1918	1,390,628
1912	935,612	1919	981,054
1913	899,830		

* "Tariff Information Surveys," U. S. Tariff Commission, 1921, Washington, D. C.

On the other hand, soda ash by the LeBlanc process, which dates back to 1791, reached a maximum yearly production of about 550,000 tons in 1879-1883. It began to decrease, as the successful operation of the ammonia process by the effort of the Solvay brothers was gradually assured. When, in 1902, the world production of soda ash by the ammonia process reached 1,600,000 tons, that by LeBlanc process was decreased to 150,000 tons, about 1/10 of the output by the ammonia process. At present, practically the whole bulk of soda ash in the world is manufactured by the ammonia process.

The earlier production in the United States where no LeBlanc soda was ever produced is shown in Table 9; more recent production figures are given in Table 10.

TABLE 10. Recent Annual Production of Soda Ash and Allied Products in the United States* (in short tons).

	1921	1923	1925	1927	1929	1933	1935	1937	1939
Total soda ash	959,593	1,707,987	1,907,791	2,037,808	2,682,216	2,317,011	2,508,859	3,037,421	2,961,632
Soda ash by ammonia process	929,448	1,674,234	1,850,013	1,974,157	2,586,304	1,585,633	1,776,470	2,205,006	2,013,264
Natural soda and soda by other processes	30,145	33,753	57,778	63,651	95,912	68,395	95,165	118,753	132,897
Total caustic soda †	238,591	436,619	497,261	573,417	758,800	686,983	759,381	968,726	1,025,011
Caustic soda by lime process	163,044	314,195	355,783	387,235	524,985	439,363	436,980	488,807	530,907
Caustic soda by electrolytic process	75,547	122,424	141,478	186,182	233,815	247,620	322,401	479,919	494,104
Bicarbonate of soda	129,331	145,316	123,472	121,449	140,234	129,273	136,556	142,161	148,610
Sal soda	69,342	68,802	63,619	55,220	62,062	......	39,439	33,064	28,668
Modified sodas	......	47,669	47,452	53,866	59,618	21,873	29,103	26,497	32,101

* From "Biennial Census of Manufacturers," Dept. of Commerce, Washington, D. C., up to 1939.
† Not including quantities of caustic manufactured and consumed by the wood pulp and textile industries.

From Table 10, it may be concluded that at present the United States alone (taking into account all forms of soda made) produces in excess of 3,000,000 tons annually. The production of electrolytic caustic in this country is increasing very rapidly on account of increased demand for chlorine. Natural soda is being produced in considerable quantities in California and its influence will soon be felt. The trade in sal soda, however, is declining consistently.

Further, in the United States as of 1940, the annual production of the five ammonia soda companies * was 3,157,000 tons, while that of the natural soda plants was over 100,000 tons, so that the total annual capacity for the United States is well over 3,000,000 tons, representing 83 per cent of the total installed capacity existing at the beginning of 1940.

Allocating by plants we obtain the U. S. capacity figures in Table 11.

TABLE 11. United States Ammonia Soda Plant Capacity.

Plants	Capacity in short tons of soda ash per day	
1. Solvay Process Co.		
Syracuse plant	2,200	
Detroit plant	2,000	
Baton Rouge plant	550	
Amherstburg plant (Brunner-Mond (Canada) Ltd.	230	
Hutchinson plant (if rehabilitated)	200	
	5,180	5,180
2. Michigan Alkali Co.		
North plant	1,500	
South plant	500	
	2,000	2,000
3. Diamond Alkali Co.	1,800	1,800
4. Columbia Alkali Corp.		
Barberton plant	1,000	
Corpus Christi plant	450	
	1,450	1,450
5. Mathieson Alkali Works, Inc.		
Saltville plant	750	
Lake Charles plant	450	
	1,200	1,200
	Total	11,630 short tons per day

The foregoing figures indicate that there is a total potential capacity of ammonia soda ash in America of approximately 4,000,000 tons annually, but that the industry has been operating at only a fraction of this potential capacity. The increase in production has been rapid and has averaged about 4 per cent each year for many years, except the last few years. Caustic soda by the lime process is made by all these works from about one-third of the soda ash produced, although it is included under

* *Chem. Met. Eng.*, **48**, 93 (1941).

and calculated as soda ash. The Solvay Process Syracuse plant, the Mathieson Alkali Saltville plant, and the Michigan Alkali and Diamond Alkali plants also make pure bicarbonate of soda, washing sodas, calcium chloride and salt.

The total world output of soda ash is estimated in Table 12.

TABLE 12. World Output of Soda Ash (in metric tons).

Year	Production by LeBlanc Process	Production by Ammonia Process	Total
1800	nil	nil	nil
1850	150,000	nil	150,000
1863	300,000	nil	300,000
1865	374,000	300	375,000
1870	447,000	2,600	450,000
1875	495,000	30,000	525,000
1880	545,000	136,000	681,000
1885	435,000	365,000	800,000
1890	390,000	633,000	1,023,000
1895	265,000	985,000	1,250,000
1900	200,000	1,300,000	1,500,000
1902	150,000	1,610,000	1,760,000
1905	150,000	1,750,000	1,900,000
1911	130,000	1,900,000	2,030,000
1913	50,000	2,800,000	2,850,000
1916	Small	3,000,000	3,000,000
1923	nil	3,500,000	3,500,000
1927	nil	4,100,000 *	4,100,000
1932	nil	5,000,000	5,000,000
1940	nil	7,000,000	7,000,000

* According to Julius Kuchner.

To aid comparison, the curves shown in Fig. 8 have been prepared.

The present annual production of soda ash in each of the various countries in the world is estimated in Table 13. These figures have been rounded off for the sake of convenience in comparison even where more accurate figures are available.

TABLE 13. Recent Ammonia Soda Production in Various Countries.

Country	Approximately Yearly Production in Terms of Soda Ash (Metric Tons)	Country	Approximately Yearly Production in Terms of Soda Ash (Metric Tons)
United States of America	3,000,000	Canada	83,000
(Natural Soda only)	(120,000)	China	80,000
Great Britain	1,500,000	Jugoslavia	70,000
(Magadi-Natural Soda		Spain	50,000
only	50,000)	Austria	45,000
Germany	1,250,000	Australia	30,000
France	710,000	India	30,000
Russia	570,000	Switzerland	30,000
Italy	387,000	Rumania	25,000
Japan	250,000	Norway	18,000
Czechoslovakia	150,000	Holland	15,000
Poland	100,000	Venezuela	2,000
Belgium	88,000		

Table 14 represents an attempt to give a list of ammonia soda plants existing in different countries in the world together with the year of their construction. The change in geographical boundaries, especially in warring countries in Europe as the result of World War II, may further
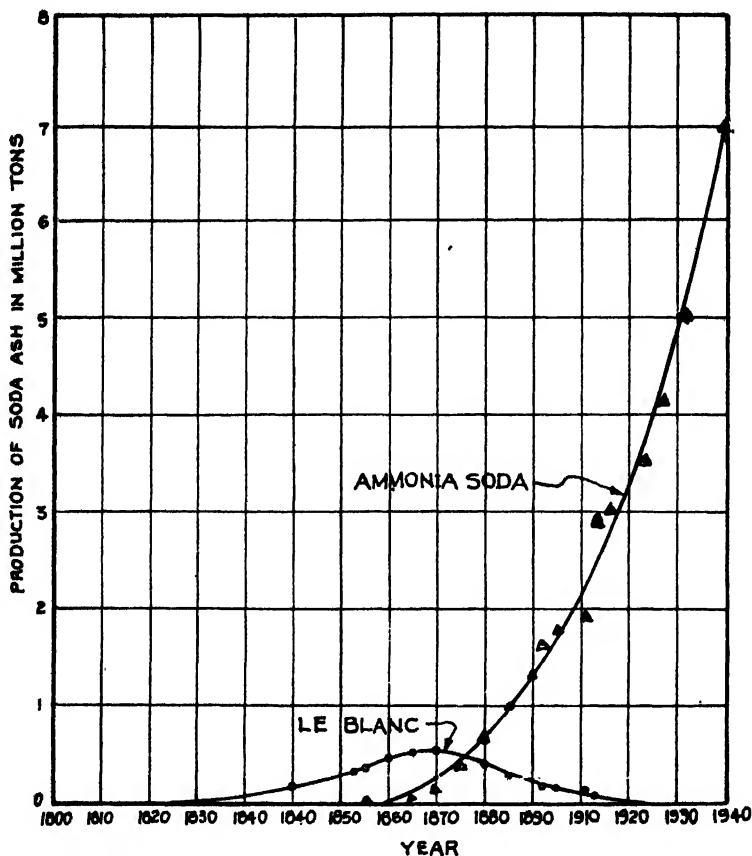
FIG. 8. Curves showing world output of soda ash from beginning to 1940.

alter the distribution of these ammonia soda plants among these countries. It is understood that such an estimate is approximate as regards the daily capacity of each plant in terms of soda ash.

Tables 13 and 14 are compiled from various sources of which a full list cannot be given here. The principal references are listed below:

G. Lunge, "Sulfuric Acid and Alkali," Vol. 3, New York, D. Van Nostrand Co.

F. Ullmann, "Enzyklopädie der technischen Chemie," Berlin, Urban and Schwarzenberg.

E. Thorpe, "Dictionary of Applied Chemistry," London, Longmans, Green & Co.

Solvay & Pennock, "Report of the 5th International Congress of
Applied Chemistry."
"Mineral Industry," 1892-1939, New York, McGraw-Hill Book Co.
"Minerals Yearbook," 1932-1939, Bureau of Mines, U. S. Dept. of the
Interior, Washington, D. C.

TABLE 14. General Survey of World's Ammonia Soda Industry.

Name and Location		When Built	Daily Capacity of Soda Ash (Tons)
United States			
Solvay Process Co.	Syracuse, N. Y.	1881	2200
	Delray, Mich.	1898	2000
	Baton Rouge, La.	1935	550
	Hutchinson, Kans. (not operating)	1908	200
Michigan Alkali Co., Wyandotte, Mich.		1893	2000
Diamond Alkali Co., Fairport, O.		1910	1800
Columbia Alkali Corp., Barberton, O.		1900	1000
(Southern Alkali Corp.) Corpus Christi, Texas		1934	450
Mathieson Alkali Works	Saltville, Va.	1894	750
	Lake Charles, La.	1935	550
Great Britain			
I. C. I. (Brunner, Mond & Co., Ltd.)	Winnington	1874	1500
	Middlewich	1889	350
	Sandbach	1875	1100
	Wallerscote	1890	700
	Lostock Gralam	1925	800
I. C. I. (United Alkali Co., Ltd.) Fleetwood		1890	400
Germany			
Deutsche Solvay-Werke	A. G. Bernburg	1883	1100
	Rheinberg	1908	400
	Wyhlen	1880	200
Kali-Chemie	Heilbronn	1900	200
	Aachen	....	150
Chem. Fabrik Kalk, Koeln-Kalk		....	150
Henkel & Cie, Duisburg		....	250
Theodor Goldschmied, Stassfurt		1883	150
I. G. Farbenindustrie, Oppau		1915	300
(And several small establishments)			
France			
Solvay et Cie	Saaralben	1885	300
	Château-Salins	1898	150
	Dombasle	1874	1200
	Salins de Giraud	1896	200
Kuhlmann, Dieuze		1875	50
Marchéville-Daguin & Cie, La Madeleine		1882	200
St. Gobain, Varangéville		1891	250
Etudes et Produits Chimiques, Mouguerre		1918	50
Russia			
Lubimoff-Solvay et Cie	Beresniki	1883	400
	Donetz	....	1000
Slavyansker, Slavyansk		....	500
Japan			
Asahi Glass Co., Ltd., Tobata (Fukuoka)		1916	600
Nippon Soda Co., Ltd., Tokuyama (Yamaguchi)		1918	800
Toyo Soda Co., Tonda (Yamaguchi)		1936	500

<div align="center">

TABLE 14. *Continued.*

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Name and Location	When Built	Approximate Daily Capacity of Soda Ash (Tons) Approximate
South Manchurian Co., Pulantien (Darien)	1937	120
Kyushu Soda Co., Kyushu	1936	100
Nippon Chisso Hyrio, Konan (Korea)	1937	100
Dai Nippon Artificial Fertilizer Co., Onoda (Yamaguchi)	1938	75
Italy		
Soc. Montecatini, Monfalcone (Trieste)	1913	300
Solvay & Cie, Rosignano	1919	800
Czechoslovakia		
Chemische Werke Aussig-Falkenau (I. G. Farben.), Nestomitz	1906	350
Chemische Werke Aussig-Falkenau (I. G. Farben.), Aussig.	1885	150
Synthesia Chemical Works, Ltd., Semtin	1934	10 *
Jugoslavia		
Solvay et Cie & Aussiger Verein { Lukavac (Bosnia)	....	200
Solvay et Cie & Aussiger Verein { Hrasnica	....	100
Poland		
Solvay et Cie { Montwy (Posen)	1881	200
Solvay et Cie { Podgorze (Galicia)	....	100
Belgium		
Solvay et Cie, Couillet	1853	250
Canada		
Brunner-Mond (Canada), Ltd., Amherstburg	1917	250
China		
Yungli Chemical Industries, Ltd. { Tangku	1921	250
Yungli Chemical Industries, Ltd. { Wutungchiao	1941	50
Spain		
Solvay et Cie, Torrelavega	1908	320
Austria		
Solvay Sodabetriebsgesellschaft, Ebensee	1885	200
Australia		
Imperial Chemical Industries, Ltd., Adelaide	1940	100
India		
Imperial Chemical Industries, Ltd., Khewra (Punjab), (under construction)	1941	80
Tata Chemicals, Ltd., Mithapur (Kathiawad), (under construction)	1941	120
Rumania		
Uzinele Solvay, Turda & Maros Ujvar (2 plants)	....	150
Switzerland		
Solvay et Cie, Zurzach	1915	100
Norway		
Norsk Hydro-Elekt., Heroja	1933	75
Holland		
Solvay et Cie, Roermond (Limburg)	1939	50(?)
Venezuela		
Comp. Anon. Ind. Quim. Nac., Maiquetia	1935	3

* All as $NaHCO_3$, by a modified Ammonia Soda process. The $NaHCO_3$ is used directly in the manufacture of $NaNO_3$.

For the recent figures, the United States Dept. of Commerce "World Trade Notes on Chemicals and Allied Products" and more recently "Industrial Reference Service: Part I, Chemicals and Allied Products" published by the Bureau of Foreign and Domestic Commerce, have proved to be an invaluable aid. Because of the peculiar tradition of this ammonia soda industry, no official figures are published by the industry nor by the government agencies with the exception of the United States. Much of the information, therefore, has to be derived from individual investigations. The foregoing figures represent the best available estimates and no strict accuracy is claimed for them. A brief summary by Harald Ahlqvist entitled "Alkali Industries Girdle the Globe" * revealed certain figures concerning soda ash production and consumption for certain countries in the world up to 1936.

In conclusion, it might be added that the International Syndicate of Solvay et Cie suffered considerable setback immediately after the World War I (1914-1918). Since that war the Russian Lubimoff plants first broke off relations with the Syndicate. Then followed the American Solvay Process Co. which severed its ties with the European Syndicate by its merger into the Allied Chemical and Dye Corporation in 1920. From that time on, all interchange of technical data and information and all confidential communications between the Russian or American alkali plants and the Solvay Syndicate and its member plants in the world ceased. Similar change of status had also to be brought about for the British plants when Brunner, Mond & Co., Ltd. was merged into the Imperial Chemical Industries, Ltd., in 1926. How much of the tie is still left between the I.C.I. and the Solvay Syndicate is a matter of conjecture. However, since that time, the International Solvay Syndicate seemed to have gradually recovered from this setback and has acquired interest in several alkali plants in certain European countries, so that today this European syndicate still owns or has interest in a total of some 26 ammonia soda plants in the world. It is to be noted, however, that independent firms outside of the Solvay combine have also multiplied very fast and have built many new plants, particularly in the United States, Japan, China, India, etc.; and the trend hereafter seems to be distinctly toward increase in the number of the independent alkali plants the world over.

* *Chem. Met. Eng.*, **43**, 278-281 (1936).

Chapter IV

Preparation of Brine: Rock Salt and Sea Salt

Salt employed in the standard ammonia soda process * is in the form of brine exclusively. The manufacture of soda ash presupposes an abundant supply of cheap salt, for the process is rather wasteful as far as the utilization of salt is concerned. The best practice in present-day soda plants does not utilize more than 75 per cent of salt and oftentimes much less. If therefore salt is not cheap, it would not be possible to operate the process successfully.

Rock salt or natural brine is generally to be preferred to sea salt on account of its higher purity; but it is now known that sea brine, after saturation by solar evaporation, can also be used. Ammonia soda plants in China and Japan are all employing sea salt. A new ammonia soda plant at Adelaide, Australia, also uses sea salt. The use of sea salt, however, is attended by difficulties, and means must be provided to get good settling for the ammoniated brine and to handle the precipitate or "mud" in the settling system with certain special provisions. Pretreatment of brine is generally recommended. The impurities (such as magnesium salts) are present in sea brine to a larger extent than in rock salt, with the result that sea brine leaves a large precipitate in the form of $MgCO_3$ in the settling system. The magnesium "mud" is rather "sticky," and if means are not provided to keep it in suspension and draw it out regularly, it will "set" and build up thick scale, plugging the whole system. Difficulties of this sort may become so serious that operation may be stopped.

Pretreatment of the brine before sending it to the system for soda ash manufacture has been employed. The reagents used in the treatment are the usual soda ash and lime. Soda ash precipitates calcium chloride and calcium sulfate in the form of calcium carbonate, whereas lime, by causticizing soda ash, yields sodium hydroxide, which precipitates magnesium chloride and magnesium sulfate as magnesium hydroxide. Purification of brine will be treated in a separate chapter and hence will not be dwelt upon here.

As we shall see later, the brine in passing through the system first acts as a scrubbing medium and then as an absorbing medium for ammonia. It finally reacts with ammonia and carbon dioxide gases, accomplishing exactly the same result as when soda and lime are added. Further the reaction takes place when the solution has been heated to 70° C. Since this reaction results naturally during the ammoniation of brine,

* A modified ammonia soda process uses solid salt in finely pulverized form.

the pretreatment of brine is often omitted for reasons of economy and expediency.

Typical analyses of rock salt and sea salt are shown in Tables 15, 16 and 17.

TABLE 15. Rock Salt (Brine). (Sp. gr. at 15° C. 1.196).

	Grams/liter	Per Cent (on dry basis)
NaCl	297.0	97.95
CaSO₄	5.15	1.70
CaCl₂	0.55	0.18
MgCl₂	0.49	0.16
Suspended matter	0.03	0.01

TABLE 16. Sea Salt (Crystals).*

	Per Cent	Per Cent (on dry basis)
Moisture	5.99	
Insoluble matter	0.82	0.890
NaCl	88.73	96.31
KCl	0.143	0.155
KBr	0.024	0.026
KI	0.186	0.202
Fe₂O₃ and Al₂O₃	Nil	Nil
CaSO . 2H₂O	1.781	1.531 (CaSO₄)
MgSO . 7H₂O	1.249	0.662 (MgSO₄)
MgCl₂ . 6H₂O	0.448	0.229 (MgCl₂)

* The sea salt has been more or less purified as the natural result of partial crystallization by solar evaporation. The original brine contains more impurities.

TABLE 17. Rock Salt from Kingman, Kansas.†

	Per Cent
NaCl	97.51
CaSO₄	1.51
Na₂SO₄	0.57
MgCl₂	0.10
Fe₂O₃	0.11
Insoluble matter	0.20

† F. W. Clarke, "Data of Geochemistry," U. S. Geol. Surv., Bulletin 770, p. 231.

The average composition of sea water is given in Table 18.

TABLE 18. Average Composition of Solids in Sea Brine.‡

	Per Cent
NaCl	77.76
MgCl₂	10.88
MgSO₄	4.74
CaSO₄	3.60
K₂SO₄	2.46
CaCO₃	0.34
MgBr₂	0.22

‡ F. W. Clarke, "Data of Geochemistry," U. S. Geol. Surv., Bulletin 770, p. 127.

Rock Salt

Rock salt for soda works is generally obtained in the form of saturated brine by pumping water under pressure to the bottom of the rock salt stratum so that it comes into contact with the salt deposit and dissolves it to saturation. Saturation is obtained by adjusting the rate of pumping. This saturated brine is either forced up to the surface by the pressure of the entering water itself, or is pumped up by means of compressed-air lift or deep-well pumps, if the rock-salt vein has crevices or is in communication with other wells so that the brine cannot be forced up under pressure. The depth of the wells varies in different localities.

Rock salt in the United States is found in great beds where it was deposited millions of years ago by the drying up of sea water in shallow lagoons which were once flooded from the sea. The salt was deposited in layers, and beds frequently covered with floods of muddy water or brine formed layers of shale, so that these beds of salt are sandwiched between many layers of shale. Other strata are formed over these beds so that most of them occur below 1000 feet.

In New York State, deposits occur at Tully. The top bed occurs at 1210 feet below the surface and is 45 feet thick. In the next 300 feet, there occur three other layers, 35, 25, and 100 feet thick, respectively. Between these beds are layers of shale of different thicknesses. At Ithaca, N. Y., the wells are 2300 feet deep, and there are also several beds of salt with layers of shale between them.

In Michigan, at Detroit and Wyandotte, these wells are 1600 feet deep with 400 feet of salt; whereas at St. Clair, the wells are from 2100 to 2300 feet deep. Some beds in the center of Michigan are said to be as much as 800 feet thick. The whole of Michigan seems to be underlaid with a great bed of salt which is perforated by wells at Detroit, Wyandotte, St. Clair, Manistee, Ludington, and many other places along the lake shore and in the interior of the state. Impure brine is found at Bay City and Midland, from which various by-products of salt are recovered.

In Ohio, at Barberton, the wells are about 2800 feet deep. Along the Ohio River, the bed is found at 5000 feet; at Pittsburgh, Pa., it is at 6000 feet. A great bed of salt extends under Lake Erie from Canada under nearly the entire state of Ohio and western Pennsylvania.

In Kansas, at Hutchinson, the wells are about 800 feet deep, and the bed 300 feet thick. This bed is nearly 100 miles wide, extending into Texas. At Carlsbad, Texas, a bed of potash, which is being mined, is found with the salt.

In Michigan, Ohio, and West Virginia, natural brine exists, but generally such brine is not saturated. Natural brine is formed by underground springs passing through the rock salt veins, or it is formed from the bittern, from which beds of salt have been deposited, in which case the brine contains many impurities which can be worked up into valuable by-products, as in Bay City and Midland, Michigan. Natural brine often

comes up almost to the surface, but sometimes remains at a great depth requiring deep-well pumps, such as Reda type pumps.

In Texas and Louisiana along the Gulf Coast peculiar deposits of salt are found in the shape of domes which seem to have been pushed up by pressure from below. These salt domes, or "plugs," are of great depth, some having been drilled to 6000 feet and still not penetrated through. Some are estimated to be perhaps 40,000 feet in thickness. These domes are of various shapes—round, oval or irregular—from a mile to three or four miles in diameter, close to the surface or down to 1000 feet, capped with a layer of limestone with sulfur under it. Frequently petroleum is found in the beds of sand between layers of clay which have been pressed upward by the movement of the dome or "plug" so as to form a reservoir for the oil. These domes have been located in conjunction with deposits of petroleum found by observations with some geophysical and electro-magnetic instruments.
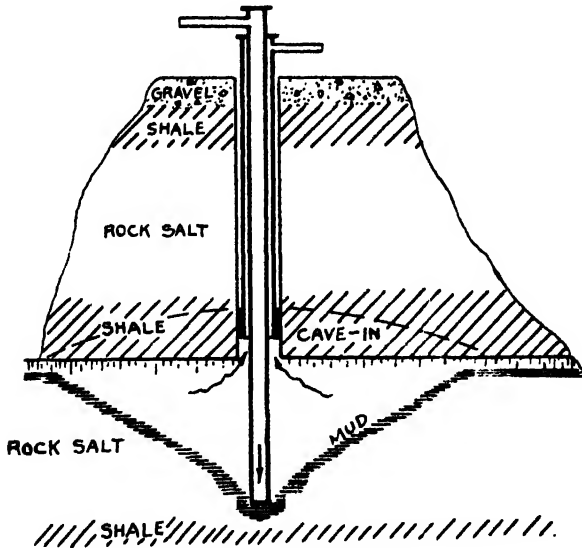
FIG. 9. Brine well.

The Solvay Process Co. discovered salt at Tully in 1896 and built a 12-inch pipe line 18 miles long from one reservoir at the wells to one at the works. In 1936, an additional pipe line, 20 inches in diameter, was added, which delivers brine by gravity with a fall of 265 feet head. A water supply from lakes, 500 feet above the highest well, provides ample pressure to elevate brine so that no pumping is required, except an air pumping plant which was used when groups of wells were connected and one of them needed repairs.

Brine wells are 6 or 8 inches in diameter, the hole being drilled clear down to the bottom of salt bed. A 10- or 12-inch steel casing is driven

through the clay or gravel into a bed of rock to cut off the surface water, and the hole is drilled inside the casing to a layer of hard rock under the water seam. The 6- or 8-inch pipe is then seated in the rock and cemented on the outside at the bottom to make a dry hole. The hole is then continued to the bottom of the salt bed. (See Fig. 9.)

A 3- or 4-inch inner tube is suspended inside the well, supported on a casing head screwed on the top of the 6- or 8-inch casing. Openings are provided into the annular space between the well and the inner tube, with valves inserted to control the water or air supply. These valves allow the water or air to be turned into the inner tube or the annular space outside, so that the tube may be cleared, when necessary, by reversing the flow.
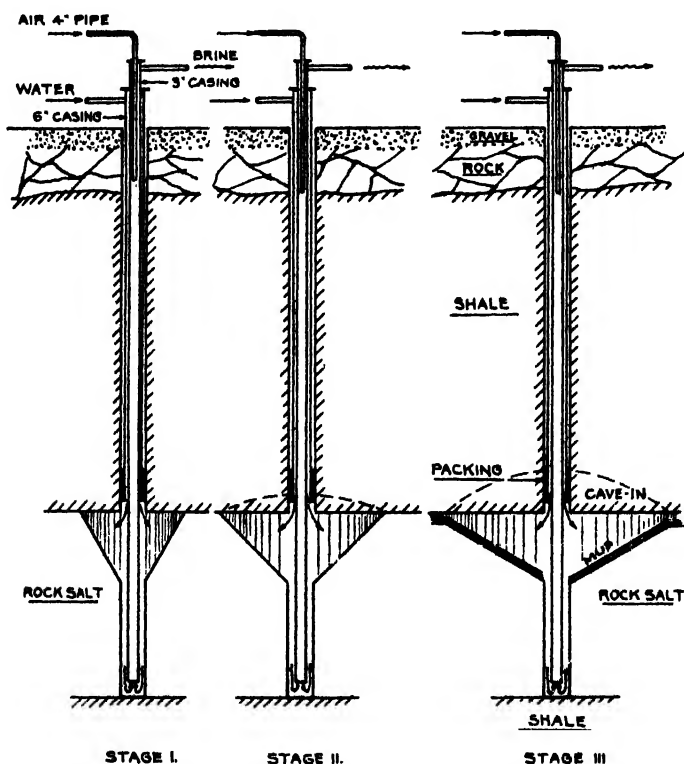
Fig. 10. Tully method.

Several methods are used in sending water down to dissolve the salt and elevate the brine. These are the New York or Tully Method, the Detroit or Kansas Method, the Trump Method, etc. For beds of salt thinner than 200 feet, the Tully method (Fig. 10) is used. The water is first turned down into the center tube and the dilute brine forced up the annular space until gradually a large cavity is formed. Then the flow is
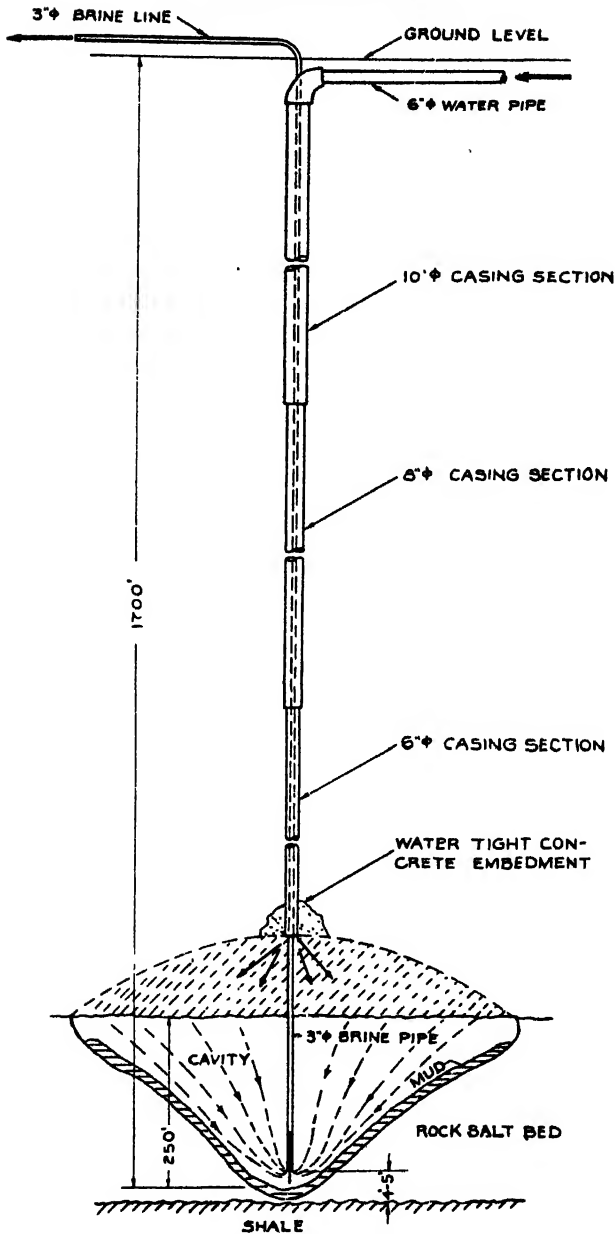
FIG. 11. Tully method well in operation.

reversed by introducing the water into the annular space so as to dissolve the salt from the top down. This is the regular production method. (See Fig. 11.) The cavity so produced gradually assumes the shape of a cone with the tip of the cone downward in the center below the lower

end of the inner tube. The reason for this is that fresh water introduced through the annular space at the top of the cavity dissolves the salt much faster at the top portion and the rate of solution decreases as the water descends, having picked up salt on its way down to the bottom of the center tube, through which saturated brine is finally forced to the surface. This explains the formation of a shallow cone-shaped cavity with the base of the cone upward. As the fresh water enters at the center of the top of the cavity, the water dissolves more salt from the center than from the outer areas; a circular arch is thus formed at the top of the cavity. This causes the base of the inverted cone to assume a spherical dome until it gradually extends to the flat shale roof, as the layer has gone to solution completely.
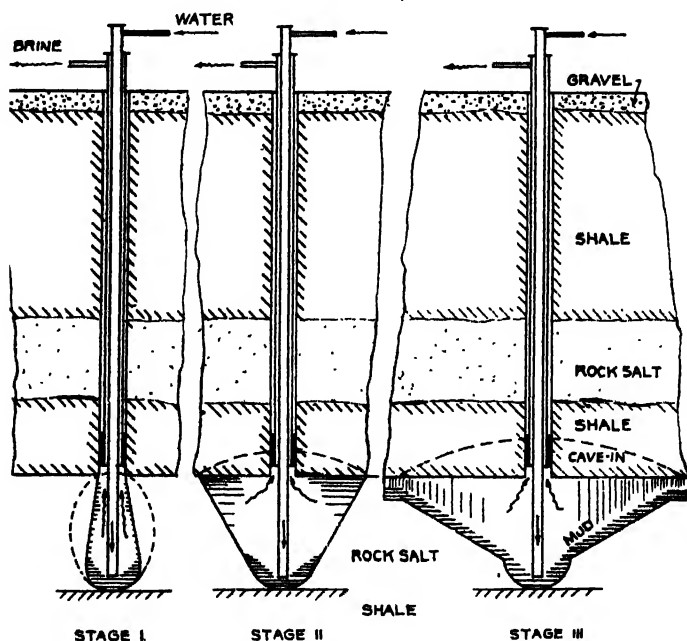
Fig. 12. Kansas method.

The cavity increases as the salt is dissolved out. When the cavity reaches a diameter such that the shale roof cannot support itself, it caves in and serious subsidence of ground has sometimes occurred. The collapse of the cavity often breaks off the center tube. The hole now has to be redrilled until the tube can be replaced. The frequency of these cavings depend on the character of the shale roof, the thickness of the salt bed, and the rate of pumping the brine. With a salt bed about 50 feet thick and ordinary shale roof, caving-in may occur as often as once in six months. At Tully with a 45-foot bed, caving-in occurred about twice a year, and today only 40 out of some 90 wells drilled remain. Mud often

collects at the shallow conical bottom up to 6 inches or more. Cleaning is an expensive operation and repairs may cost $1500 each time the inner tube is cut off.

If the bed of salt is over 200 feet thick, it is possible to obtain saturated brine by forcing water down the inner tube to the bottom of salt bed and making brine come up the annular space. This is the Detroit or Kansas Method (see Fig. 12). The pear-shaped cavity will enlarge; but due to the deposition of mud at the bottom—"blanketing"—the bottom of the cavity is gradually covered with soft mud and protected from solution, so that solution of salt takes place much faster at the top than at the bottom. Consequently an inverted, cone-shaped cavity is again formed. No caving will occur for some time; but when a large diameter has been dissolved off at the top, caving-in will eventually take place.

Deep brine wells sunk into one of the Louisiana salt domes, or "plugs," give a very long life per well.

The detailed method of operation of brine wells depends on the nature of the salt stratum being exploited. Where the strata are relatively thin, a modern technique adds to the life of a well by avoiding the caving-in of the weaker shale or earth strata overlying the salt beds, by keeping a cushion of air or oil under high pressure above the dissolving water. A strong roof over the salt cavity is thus maintained. If the salt strata are near the surface and there is difficulty in preventing infiltration of ground waters, the brine is pumped to the surface by an air lift. By controlling the rate of pumping, the brine may be brought to almost complete saturation. By the addition of strong brine from other wells, some weaker brine is utilized for the manufacture of soda. Very weak brine resulting from well development may not be disposed of in fresh-water streams without endangering fish life in the stream and all the plant life irrigated by it. Such weak brine is generally utilized in place of fresh water in operating the regular production wells.

Since the capacity of a well depends on the area of salt surface in contact with water, a new well naturally has a low capacity and is likely to produce weak brine. This is particularly true if the salt beds are thin. It is therefore necessary to anticipate the life of a well and have a number of wells under development for use several years hence. The development of new wells in a shallow salt stratum can be accelerated by circulating abnormally large volumes of water or drilling several wells in a row abnormally close to each other, so that their cavities may soon join together and become connected, after which these wells may be operated as a single well with water going down one hole and brine coming up the other hole at the extreme end.

From the above it should be clear how the cavity becomes cone-shaped in the inverted position. The cavity first is in the shape of a steep hole, which gradually widens out at the top until the sides get so flat that the mud in the water and the impurities in the salt settle on the bottom and blanket it. Consequently, the salt at the bottom will not

dissolve except around the edge of the cavity and on the top. As soon as the cavity reaches 125 or 150 feet in diameter, the rock caves and still further blankets the floor. This caving may cut off the pipe so that the well has to be rebuilt through the debris and a new pipe introduced. On thicker beds, 200 feet thick or more, brine is obtained by putting down water through the central pipe and the water drives the brine up. This first results in a spherical cavity at the bottom around the pipe, but deposition of the mud soon covers the bottom. Then the cavity can widen only at the top. This gradually becomes a shallow conical pit with blanketed flat slopes toward the center and with curved roof over the top. Thus, again the cavity becomes an inverted cone with a dome-shaped base upward.
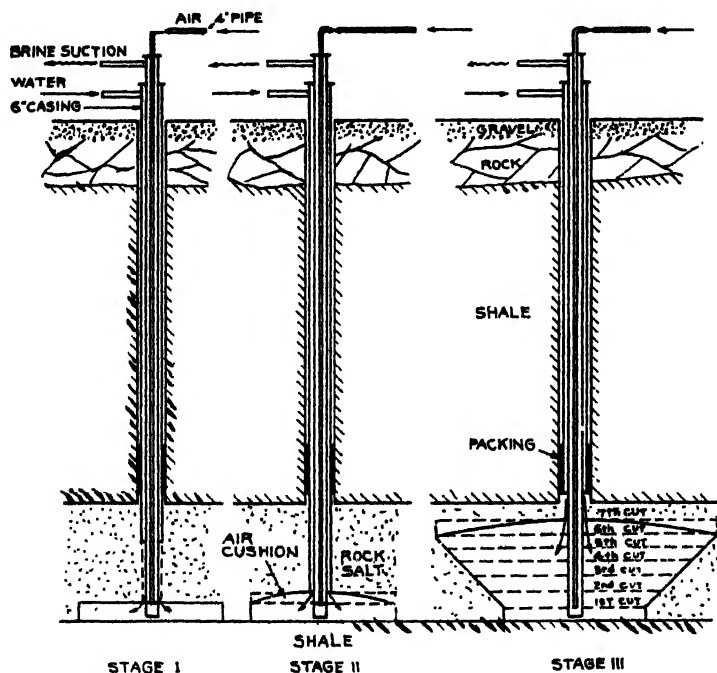
FIG. 13. Trump's method.

In 1929 Mr. Edward N. Trump, of Syracuse, N. Y., invented a method of undercutting the beds of salt by holding water at the bottom of the salt bed to a depth of about 4 feet above the bottom, controlled by drilling holes in the center tubes 4 feet from the bottom. Water for dissolving the salt is sent in through the annular ring as in the Tully method. Air is introduced with the water, which carries it down in bubbles which are gradually absorbed, while the surplus of the air escapes through the holes. Water in the salt bed is confined by air which forms a cushion above it, thus preventing contact between the water and salt at the top.

This makes a flat cavity of a large diameter horizontally, and brine gravitates to the bottom of the center tube and is forced up with the air through it. Fresh water holds air up to 1.7 per cent by volume, but saturated brine holds only about $\frac{1}{4}$ of this amount. The air dissolved in the water is thus gradually liberated, as the water picks up salt to saturation, forming bubbles that lighten the brine and act as a partial air lift. Fig. 13 shows progressive stages of undercutting in the Trump method. The undercut is 4 feet high, and a flat cavity some 300 feet in diameter may be obtained in 12 months' time. After the undercut has attained a desired diameter, air is lifted off and the water level raised, to dissolve the top portion of salt from below. Thus a larger cavity of undercut with a dome-shaped top is formed, and so on, until a large inverted frustum of a cone is obtained, capable of producing large volumes of saturated brine. Note that as in the Tully method, where water is admitted at the top, the cavity at the top also assumes a spherical dome shape by the solution of salt by water from below. With the cavity of 300 feet in diameter at the top, the well will produce 100 gallons of saturated brine per minute, whereas by the Tully method, the well will produce only 50 gallons of saturated brine a minute, and may cave in when the top diameter of the cavity attains 125 feet. It is possible to undercut a still larger diameter than 300 feet by the Trump method by placing wells in rows at 700 feet apart.

In May, 1934, the Solvay Process Co. of Syracuse, N. Y., introduced another method for dissolving the salt from salt beds. Instead of using a single hole for sending in water and elevating out brine, two or more holes are drilled; through one of these water is sent down, and through the other brine is removed either by pumping, air lift, or other means. This is no different from the method used in the Province of Szechwan, China, a number of years ago. At Tawenpao in the Tzeliutsing district in Szechwan, as many as 36 such wells scattered widely apart are grouped together. Water is sent in through one of these wells and brine is pumped out by long buckets operated by a cable hoist from six of the other wells in daily rotation.

Natural brine almost up to saturation occurs in Cheshire, England. In southeastern Ohio and in West Virginia, natural brine is found in a less concentrated form. In Szechwan, China, many natural brine wells exist, but the brine obtained is of two forms: "yellow brine" containing from 8-12 per cent NaCl from the shallower wells (1200-1800 feet), and "dark brine" containing 12 to 18 per cent NaCl from wells somewhat deeper (1500-2200 feet). Salt beds so far are found only at 3100-3300 feet in the Tawenpao district where the method patented by the Solvay Process Co. in 1934 has been in use for decades.

In Germany, natural brine is obtained in rather dilute form in many places in central Germany, notably Bad Duerrenberg, Schoenebeck, etc., where such weak brine is concentrated in rows of towers packed with twigs several kilometers long. Weak brine is sprayed over the twigs, allowed to trickle down from the top and concentrated by evaporation

with the aid of solar heat and winds. Such structure when viewed from afar has all the appearance of a great wall in a Tartar City!

There are a great many salt deposits throughout the world. In England, they exist in Cheshire and Lancashire Counties. In Germany, there are the famous Stassfurt deposits and others at Bernburg, etc. In the United States, they occur in Michigan, New York, Ohio, West Virginia, Kansas, Texas, Louisiana, etc. It is in such places that the ammonia soda industry has been built up.

In the early days of the American ammonia soda industry, natural brine used to be saturated with mined rock salt shipped into the plant. Since the development of the deep brine-well technique, no American ammonia soda plant uses solid salt. Such brine is often transported over a long distance to the ammonia soda works. The Solvay Process plant at Syracuse, N. Y., pipes its brine over a distance of 18 miles in 20-inch pipes, as mentioned before. Striking recent examples are the 60-mile pipe lines for the Southern Alkali Corp. at Corpus Christi, Texas, and the tremendous Mississippi River crossings for the Solvay Process plant at Baton Rouge, La.

The distribution of salt production in the United States as of 1938 is shown in Table 19.

TABLE 19.   Distribution of Salt Production in the United States (1938).*
Total production for the year 1938=8,025,768 short tons, including
partially that consumed in the caustic soda manufacture.

	Per Cent
Michigan	25.85
New York	21.40
Ohio	18.54
Louisiana	11.93
Kansas	7.46
California	4.36
Texas	4.04
West Virginia	1.62
Utah	0.77
Other States	3.82

* Minerals Yearbook," 1939, Bureau of Mines, U. S. Department of Interior.

Some typical analyses of rock salt brines are shown in Table 20.

TABLE 20.   Typical Analyses of Rock Salt Brines.

	Wyandotte, Mich. Sp. gr. 1.20	Saltville, Va. 1.196 at 15° C.	Tawenpao, Szechwan, China 1.199 at 23° C.	Cheshire, England (Natural Brine)
	Grams per liter			
NaCl	303.6	297.0	297.84	300.0
CaSO$_4$	4.8	5.15	4.774	4.0
MgCl$_2$	1.6	0.49	1.676	0.6
MgSO$_4$	....	....	0.758	0.7
Na$_2$SO$_4$	nil	....	nil	....
CaCl$_2$	....	0.81	nil	....
CaCO$_3$	....	0.15	. ..	0.2

* Stanley Smith, Martin's "Industrial Chemistry, Inorganic," Part II, Vol. I, p. 304, London, Crosby, Lockwood & Son.

Sea Salt

Sea salt is obtained by solar evaporation of the weak brine from the sea. Flat grounds near the seacoast which are low enough so that the tide can be conducted in by canals, and which have dense clay beds, make good evaporation bottoms. The sea water is concentrated on the flat open fields or clay vats, generally very shallow, by the agencies of solar heat and sea breezes. Localities on the seacoast with a high rate of evaporation of water, *e.g.*, 5 to 10 mm. for 24 hours, are best suited for solar evaporation. To circulate the sea water from evaporating fields to the creek and back from the creek to the fields to hasten evaporation, pumps usually driven by windmills are employed. When brine has been thus concentrated up to the crystallization point, it is pumped to crystallizing fields or pans (similar to evaporating fields, only shallower), where, on further evaporation, crystals of salt separate out on the bottom. On these crystallizing fields, the brine is less than 6 inches deep. The salt crystals are raked out by hand from the smooth bottom of such fields. If the salt is not contaminated by dirt through handling, etc., there is seldom over ½ per cent of clay or insoluble matter in it when received at the works. The amount of the impurities included in the crystals will depend upon the size of crystals and the method of preparation.

The procedure according to one practice is as follows: Sea water is conducted in at high tide, or sent in by means of pumps, through canals leading from the coast to the salt fields. The sea water is stored in one or more large reservoirs or ponds, and a system of canals is provided connecting these ponds with a number of concentrating fields which are about 80 feet wide by 120 feet long by 6 inches deep, and here the brine is brought to about 18° Bé. From the concentrating fields, the brine is led in small canals to the crystallizing fields which are about 40 feet wide by 60 feet long by 5 inches deep. This transfer of brine from the reservoirs to the concentrating fields and from the concentrating fields to the crystallizing fields is effected usually by windmills. In the crystallizing fields, the brine is brought to 26° Bé and allowed to crystallize. The crystals at the bottom are raked off with long wooden rakes, collected, and stored in a common spot where they are allowed to stand so that impurities of magnesium chloride, etc. are drained off. By washing the salt crystals with saturated brine in the fields and draining, most of the impurities can be washed off and the salt thus obtained contains 90-92 per cent NaCl.

For the location of such solar evaporation salt fields, the following requirements must be met:

(1) The sea adjoining the land must be in the shape of a bay or a gulf, not directly subject to any ocean currents, and into which no large rivers or fresh-water bodies from the land empty, so that local sea water may possess a high salt content.

(2) The coastal plan must be flat, open, low and not hilly, affording large areas for concentrating the brine by solar evaporation and having more or less constant breezes to aid evaporation.

(3) The locality must not be subject to heavy precipitation or high humidity, so that a high rate of evaporation may be maintained, especially during the warmer seasons.

With the foregoing pre-requisites, it is not difficult to arrange for large clay vats or concentrating fields having a dense smooth bottom for holding the brine and to install numerous windmills for pumping and circulating the brine.

Besides salt ($NaCl$), sea brine contains many impurities. Fortunately, crystallization of salt by solar evaporation is also a means of purification, i.e., freeing the sodium chloride from impurities. Therefore, it is to be expected that the bittern left after crystallization would have a higher content of these impurities. Table 21 shows a chemical analysis of the main impurities contained in a somewhat diluted bittern.

TABLE 21. Composition of Bittern.

	Per Cent by Weight
$NaCl$	14.16
$MgCl_2$	4.64
$CaSO_4$	0.51
$MgSO_4$	0.48

The other impurities were not determined.

Within recent years, manganous sulfate has been used on brine fields to obtain better and coarser crystals, as the result of which large clusters of crystals of sodium chloride are formed in the crystallizing fields, yielding directly a crop of salt crystals containing as high as 95-96 per cent $NaCl$ with a fraction of one per cent of magnesium and calcium salts respectively left in the salt. The proportion of manganous sulfate used is about 0.06 per cent on the weight of the saturated brine, and may be reduced to one part per 50,000 by weight if the bittern is used over again with the fresh brine repeatedly. No manganese salts are found in the salt crops obtained. The crystals are large and hard and resemble weathered salt in dryness but they are in clusters. The yield of salt from the brine is also increased by about 10 per cent. One crop gave the analysis shown in Table 22.

TABLE 22. Analysis of Crude Sea Salt Obtained from Sea Brine with Addition of Manganous Sulfate.

	Per Cent
$NaCl$	96.89
$CaSO_4$	0.57
$MgCl_2$	0.17
$MgSO_4$	0.03
Insoluble Matter	0.33
Water (by. diff.)	2.01

The content in magnesium salts is remarkably low (cf. ordinary sea salt analysis, Table 16). The manganous sulfate is in the form of a

crude bluish-gray powder, known in the trade as "Mangan Crystallizer." One commercial sample of the manganous sulfate used for this purpose (a grayish dry powder) has the analysis shown in Table 23.

TABLE 23. Composition of Crude Manganous Sulfate Used as Crystallizing Assistant.

	Per Cent
$MnSO_4$	81.52
$CaSO_4$	0.37
$MgSO_4$	0.79
Fe_2O_3	1.04
Al_2O_3	0.02
SiO_2	7.70
Silicates	1.20
Carbon	2.20
Moisture	5.03
Total	99.87

As shown above, sea salt contains as impurities considerable proportions of magnesium and calcium salts. But the most economical method is not to work the brine for solid salt and then dissolve it again to make saturated brine for use in the soda works, but to use the strong brine directly from the evaporating fields, adding only what is necessary to bring it to full saturation. In this case, however, all the impurities present in the sea water are retained in the saturated brine thus obtained, and the difficulties of mud formation in the settling system, as described above, are greatly enhanced. Hence pretreatment of the brine is essential. To guard against undersaturation of brine direct from salt fields, means should be provided to bring the brine to full saturation by dissolving in it solid salt in a rotary dissolver installed at the works.

Saturated brine has a specific gravity of 1.204 at 15° C., but impure brine containing large amounts of dissolved salts has a little higher specific gravity reading. Theoretically, pure saturated brine should contain 318 grams per liter of sodium chloride.

Table 24 gives the composition of two grades of crude sea salt, representing the low and high grades. The high grade is produced by washing the crystals with the saturated brine and draining, as mentioned above.

TABLE 24. Composition of Crude Sea Salt.

Low Grade	Per Cent	High Grade	Per Cent
Insoluble matter	0.58	Insoluble matter	0.24
NaCl	84.60	NaCl	89.83
$CaSO_4$	1.02	$CaSO_4$	0.61
$MgCl_2$	2.56	$MgCl_2$	1.49
$MgSO_4$	0.81	$MgSO_4$	0.40
Water and undetermined substances by diff.	10.43	Water and undetermined substances by diff.	7.43

The data given in Table 24 represent the composition of fresh crops from crystallizing fields. If the salt after harvesting is stored in mounds of thousands of tons for a year or more, by the natural process of weathering, much of the impurities (especially $MgCl_2$) is dissolved out and eliminated. The composition would then be as shown by the analysis in Table 25.

TABLE 25. Composition of Weathered Crude Salt after Storage for 12 Months.

	Per Cent
Insoluble matter	0.64
NaCl	92.29
CaSO₄	1.17
MgCl₂	0.44
MgSO₄	0.12
Water and undetermined substances by diff.	5.34

Table 26 gives the rates of solar evaporation at San Francisco Bay, U. S. A., and at Tangku, China. The figures represent inches of water evaporated during the month.

TABLE 26. Evaporation in Inches.

Month	* San Francisco Bay, Cal., in 1911	Tangku, China in 1920
January	....	2.63
February	....	3.43
March	....	5.65
April	3.38	8.21
May	5.31	10.28
June	6.62	11.96
July	7.81	12.10
August	7.81	13.09
September	4.94	8.00
October	2.94	8.06
November	....	4.38
December	....	2.77
Total	38.81 (for 7 months)	90.56

* "Technology of Salt Making in U. S." W. C. Phalen, Bur. Mines Bull. 146, p. 41.

The annual rate of evaporation at Searles Lake, Calif., is 72 inches.*

To give some idea of the world production of salt, it may not be out of place to give here statistics compiled by the Bureau of Mines, the United States Department of the Interior, for the year 1940.

* Chapman, L. W., *Chem. Met. Eng.*, 24, 687 (1921).

TABLE 27. World Production of Salt, 1934-38, by Countries, in Metric Tons.

(Compiled by M. T. Latus)

Country [1]	1934	1935	1936	1937	1938
North America:					
Canada	293,960	324,975	355,486	415,994	398,013
Costa Rica	3,330	3,500	3,500	4,287	4,740
Guatemala	2,913	2,073	8,053	12,610	10.465
Mexico	(2)	57,746	101,628	82,876	107,701
Panama	4,947	5,541	4,385	6,898	3,332
United States:					
Rock salt	1,735,600	1,595,949	1,823,050	1,841,967	1,725,330
Other salt	5,169,921	5,595,173	6,186,384	6,541,795	5,547,321
West Indies:					
British:					
Bahamas [3]	3,175	545	....	5,003	4,830
Leeward Islands [3]	1,357	....	....	....	....
Turks and Caicos Islands [3]	18,063	28,803	41,899	50,833	35,578
Cuba	20,964	36,921	34,339	36,287	35,217
Netherland [3]	6,479	3,781	2,285	2,337	2,013
South America:					
Argentina [4]	194,443	234,441	247,433	290,084	264,150
Brazil	280,573	277,583	494,119	708,714	859,222
Chile	31.210	36,453	47,232	36,697	(2)
Colombia	181,052	181,613	171,455	164,636	(2)
Ecuador ·					
Rock salt	114	119	138	138	(2)
Other salt	28,902	32,039	16,632	13,800	13,800
Peru	34,343	35,397	36,110	39,010	34,307
Venezuela	28,357	53,225	25,128	26.298	22,658
Europe:					
Bulgaria:					
Rock salt	6,138	5,330	7,008	9,745	10,242
Other salt	48,722	36,629	47,000	43,602	66,258
Czechoslovakia	147,299	163,843	172,647	165,898	174,000
France:					
Rock salt and salt from springs	1,673.280	1,604,860	1,711,060	1,847,170	1,264,230
Other salt	398,070	356,650	202,040	490,906	346,046
Germany:					
Rock salt	2,024,194	2,077,316	2,383,825	2,757,242	2,694,984
Other salt	509,316	561,588	574,489	608,046	585,326
Austria:					
Rock salt	864	1,257	712	908	786
Other salt	163,732	198,209	191,294	169,883	93,576
Greece	107,696	113,980	74,447	102,285	102,057
Italy:					
Rock salt	393,306	483,436	499,798	603,798	613,870
Other salt	576,742	671,084	770,333	952,655	885,205
Malta	2,235	2,032	1,930	1,829	1,523
Netherlands: Rock salt	74,759	70,963	76.271	132,430	164,266
Poland	506,883	515,094	466,525	602,746	642,875
Portugal [3]	56,511	81,965	73,944	4,633	6,096
Rumania:					
Rock salt	308,723	308,921	283,389	308,882	351,723
Other salt	....	1,542	1,750	2,077	1,842
Spain:					
Rock salt	160,023	(2)	(2)	(2)	(2)
Other salt	602,308	(2)	(2)	(2)	(2)
Switzerland	81,596	79,757	81,177	81,969	84,049
U. S. S. R.	[5]3,544,000	[5]4,349,500	(2)	(2)	(2)
United Kingdom:					
Great Britain:					
Rock salt	17,650	16,571	17,569	18,666	19,974
Other salt	2,528,634	2,713,377	2,845,242	3,101,511	2,651,939
Ireland, Northern:					
Rock salt	3,533	3,282	3,175	4,254	2,362
Other salt	10,500	10,199	12,297	8,818	5,757
Yugoslavia	41,922	43,549	45,205	46,323	52,634
Asia:					
Aden	361,119	345,119	361,098	360,866	282,510
Burma	37,569	40,729	32,790	54,677	39,319
Ceylon	63,449	41,612	40,332	38,815	36,490
China [6]	3,220,000	3,000,000	3,000,000	3,000,000	3,000,000
Chosen [7]	138,000	138,000	138,000	138,000	138,000
Cyprus [7]	3,000	3,000	3,000	3,000	3,000

[1] In addition to the countries listed salt is produced in Bolivia, Gold Coast, Madagascar, and Southern Rhodesia, but figures of production are not available.
[2] Data not available.   [3] Exports.   [4] Railway shipments.
[5] Output of U. S. S. R. in Asia included with. U. S. S. R. in Europe.
[6] Includes Manchuria.   [7] Estimated annual production.

TABLE 27.—(Continued)

Country [1]	1934	1935	1936	1937	1938
India:					
British:					
Rock salt	182,047	181,214	175,020	190,103	191,395
Other salt	1,596,531	1,593,593	1,369,861	1,516,984	1,372,979
Portuguese	209,219	160,681	24,047	26,095	29,527
Indochina	160,536	203,210	192,237	193,558	193,050
Iraq	8,000	7,045	2,804	1,810	7,907
Japan:					
Japan proper [8]	676,302	604,442	518,859	535,775	(2)
Taiwan	191,577	149,375	189,777	210,471	(2)
Netherland India	92,370	102,076	107,449	75,780	[9] 74,411
Palestine:					
Rock salt	859	867	755	727	444
Other salt	9,389	10,376	8,058	11,717	8,065
Philippine Islands	(2)	(2)	53,471	48,905	(2)
Syria [7]	10,000	10,000	10,000	10,000	10,000
Thailand [8]	126,565	138,504	44,505	132,899	156,268
Turkey	190,602	214,688	220,500	262,226	247,293
U. S. S. R.	(5)	(5)	(5)	(5)	(5)
Africa :					
Algeria	42,885	67,990	62,400	63,767	74,630
Belgian Congo	888	894	920	1,004	1,013
Canary Islands [7]	2,000	2,000	2,000	2,000	2,000
Egypt [3]	288,470	257,104	237,570	276,735	284,949
Eritrea	96,000	2,380	62,000	(2)	(2)
Ethiopia: Rock salt	10,000	10,000	10,000	10,000	10,000
French West Africa	1,200	381	748	643	51
Kenya Colony	1,760	2,845	....	....	3,250
Libya (Italian Africa):					
Cyrenaica [7]	10,000	10,000	10,000	10,000	10,000
Tripolitania [7]	20,000	20,000	20,000	20,000	20,000
Mauritius [7]	1,500	1,500	1,500	1,500	1,500
Morocco, French	1,064	1,194	11,207	814	909
Nigeria [7]	400	400	400	400	400
Portuguese East Africa	1,689	3,436	2,520	2,605	6,448
Portuguese West Africa (Angola) [7]	25,000	25,000	25,000	25,000	25,000
Somaliland :					
British [3]	3,312	2,655	1,509	950	353
French [3]	35,497	76,500	21,985	85,273	(2)
South-West Africa: Rock salt	2,800	5,021	3,822	4,113	5,071
Sudan, Anglo-Egyptian	24,421	26,534	27,027	34,553	37,532
Tanganyika Territory	7,418	6,916	8,574	8,723	10,169
Tunisia	86,966	79,689	129,000	129,708	129,287
Uganda	4,950	1,590	3,405	3,133	3,169
Union of South Africa	83,233	87,261	97,904	106,338	(2)
Oceania:					
Australia :					
South Australia	62,063	79,255	67,391	74,739	76,013
Victoria [10]	46,613	48,356	(2)	(2)	(2)
Western Australia	2,713	(2)	4,295	3,729	3,850

[8] Year ended March 31 of year following that stated. The figures do not include output from salt beds which, although situated on Government beach lands, have no fixed areas.

[9] Incomplete data.   [10] Year ended June 30 of year stated.

Chapter V

Purification of Brine

Salt used in the ammonia soda industry is seldom pure and may have many constituents besides sodium chloride, such as sodium sulfate, sodium iodide, sodium bromide, calcium chloride and sulfate, magnesium chloride and sulfate, potassium chloride and sulfate, iron, manganese, clay and sand. The amount of these impurities varies with the source of the salt supply. For the ammonia soda industry, salt may come from one of the following sources:

1. Rock salt or rock-salt brine (artificial brine)
2. Natural brine
3. Sea salt
4. Sea brine (concentrated to saturation)

Rock salt is generally fairly pure, frequently containing over 98 per cent NaCl. As described in the previous chapter, it occurs underground, and is obtained either by mining or by sending water down a hole to dissolve the salt, and forcing saturated brine up by pumping, by air-lift, or by the pressure of the entering water itself. Such brine is known as rock-salt brine or artificial brine, and is generally very pure. Gypsum is the chief impurity in rock salt, and magnesium is present only in smaller percentages. Pretreatment of brine by addition of certain reagents to the water before it is pumped into the wells, thereby using the rock salt cavity as a settling reservoir, has been suggested, but so far has not been practiced. However, some natural purification takes place due to the alkalinity of the water used and to the insolubility of certain impurities and dirt which settle at the bottom of the cavity, causing "blanketing." (See Chapter IV under Rock Salt.)

Natural brine occurs underground and exists either as a rock salt bittern or as brine formed by the underground water flowing through salt strata. It is generally not so pure as rock salt or rock-salt brine, especially when it exists as a natural bittern, such as the natural brine obtained at Bay City or Midland, Michigan. Moreover, natural brine is seldom obtained in a completely saturated condition. The best natural brines have only about 95-97 per cent saturation. Other natural brines are very weak, some having only 6-12 per cent NaCl. Such brine must be concentrated by means of steam evaporators or grainers, by solar heat, or by the fortification with rock salt, before it can be used in the ammonia soda industry. Many ammonia soda plants use natural brine, notably the I.C.I.'s plant in Cheshire, England.

Sea salt is generally obtained by solar evaporation; besides sodium chloride the crystals contain sodium sulfate, calcium sulfate and chloride,

magnesium sulfate and chloride, etc. It may be obtained in abundance and cheaply along the sea coast, where climatic and geographical conditions are favorable. It contains more impurities than rock salt and more magnesium relative to calcium in the impurities. It generally requires pretreatment for the ammonia soda manufacture.

Sea brine is a saturated brine obtained directly from salt fields where sea water is concentrated by solar evaporation merely up to saturation, from which solid salt has not been allowed to crystallize. The brine will contain all the impurities in the sea water and have far more impurities than rock salt or sea salt. Pretreatment is necessary before it is used in the ammonia soda process. This form of brine, however, is very economical and does not require the roundabout method of evaporating sea water to crystallize out solid salt and then re-dissolving the salt crystals to make brine. It may be necessary to add some solid salt to it for fortification, to guard against undersaturation. When sea brine is obtainable in abundance in this way, with a suitable means of pretreatment it forms a very economical raw material for ammonia soda manufacture.

Pretreatment of brine for the ammonia soda process is now more generally practiced than heretofore. This consists of treating the brine to eliminate calcium and magnesium before it is sent to the different washers, and finally to the ammonia absorber. It eliminates the formation of scale or sludge, consisting of calcium carbonate and magnesium carbonate and/or hydroxide in the absorber system, which causes obstruction in the passages, plugging in the pipe lines, clogging in the settling vats, and many disagreeable operational difficulties. Further, sludge formation incurs losses of ammonia and salt. Because of the necessity of frequent change-overs of the apparatus and the cleaning thereof, it requires labor and time, and causes loss of production. Also, some impurities, notably magnesium, may find their way to the finished product, giving cloudiness or insoluble matter in the soda solution. Hence present practice generally resorts to some method of purifying the brine before use.

There are several methods of treating brine, of which the more common ones may be enumerated here:

(1) Treatment with ammonia and carbon dioxide gas.
(2) Treatment with lime, and ammonia and carbon dioxide gas.
(3) Treatment with lime and soda ash.
(4) Treatment with lime and sodium sulfate (followed by ammonia and carbon dioxide gas).

(1) **Treatment with ammonia and carbon dioxide gas.** This method of treatment is really a part of the ammonia soda process and will be dealt with fully in Chapter VII, "Ammoniation of Saturated Brine." It eliminates calcium and magnesium by means of NH_3 and CO_2 in hot solution. The difficulty lies in the removal of the sludge from the settling vats and in the plugging of the piping and settling system. This difficulty is aggravated by the fact that such treatment must be done in a closed system under a partial vacuum to avoid loss of ammonia. Besides the

necessity of guarding against the loss of ammonia, the disposal of mud from the strong ammoniated brine by pumping it to the distiller is accompanied by a considerable loss of salt. This method is uneconomical when there are large amounts of impurities, such as in sea salt. It also calls for a special provision in the absorber-vat system and in the arrangement of the washers and absorbers. However, the treatment is carried out in the hot condition prevailing in the ammonia absorber, and has a most favorable condition for settling. The reactions are as follows:

$$Mg^{+} + 2NH_4OH \rightarrow Mg(OH)_2 + 2NH_4^{+}$$
$$Ca^{++} + (NH_4)_2CO_3 \rightarrow CaCO_3 + 2NH_4^{+}$$
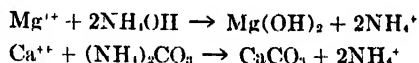
But it was found that in the presence of CO_2, magnesium is apt to come down as a carbonate or basic carbonate instead of as hydroxide, and also as a double salt $(NH_4)_2CO_3 . MgCO_3 . 4H_2O$, or as a triple salt, $NaCl . MgCO_3 . Na_2CO_3$, along with other salts, thus causing further loss of salt (NaCl) as well as of $(NH_4)_2CO_3$ and Na_2CO_3 from the ammoniated brine. (See Chapter VII, "Ammoniation of Saturated Brine.") Moreover, in place of calcium and magnesium salts, the corresponding ammonium salts are formed in the ammoniated brine, which may lower the decomposition of NaCl in the columns. Hence this method is not economical when the raw brine contains high calcium and magnesium impurities, besides the attending operational difficulties.

A modified form of this treatment is the use of large settling vats with closed top and conical bottom, each provided with a stirrer and treatment of brine in these vats with ammonia gas from the distiller or from the weak liquor still. The brine is thus partially ammoniated and the impurities of calcium and magnesium are allowed to settle off in these vats. The clarified brine is then sent to the absorber. In this way, brine is pre-ammoniated and settled before it passes through the absorber. This eliminates most of the impurities in the brine before it reaches the absorber and thus prolongs the service life of the absorber system. Such a method is in common use in the alkali plants on the Gulf Coast of the United States.

(2) Treatment with lime and ammonia and carbon dioxide gas. Advantage is taken of the fact that magnesium is very readily precipitated by $Ca(OH)_2$ even in cold brine. Using a theoretical quantity of lime, it is possible to eliminate 97-99 per cent magnesium from the brine this way, and the precipitate may be settled off by decantation. The resulting brine contains calcium equal to the amount originally present in the brine plus what was added for the elimination of magnesium.

$$Mg^{+} + Ca(OH)_2 \rightarrow Mg(OH)_2 + Ca^{++}$$
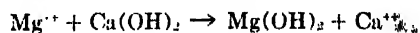
Since it is known that calcium can be readily precipitated as $CaCO_3$ and settles more or less readily, and since calcium carbonate mud does not form the kind of sticky, hard scale as does magnesium mud, it can be drawn from the settling vats. Therefore, the idea underlying this treat-

ment is first to remove the troublesome magnesium and later to remove all the calcium by the regular ammoniation process.

$$Ca^{++} + (NH_4)_2CO_3 \rightarrow CaCO_3 + 2NH_4^+$$
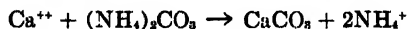
Although this does not form a double or triple salt in the mud from the ammoniated brine, it has the same objection of leaving much fixed ammonia in the resulting ammoniated brine. The treatment is particularly good for sea salt which contains high magnesium.

(3) **Treatment with lime and soda ash.** As has been mentioned above, the removal of calcium and magnesium from the raw brine by the ammonia and CO_2 treatment results in the formation of an equivalent amount of ammonium salts in place of calcium and magnesium salts in the resulting brine. This substitution of ammonium salts for calcium and magnesium salts, when present in large quantities, will interfere with the decomposition of salt by ammonium bicarbonate in the columns. It is therefore preferable to introduce soda ash in place of ammonium carbonate for the elimination of calcium after the precipitation of magnesium by lime.

$$Ca(OH)_2 + Mg^{++} \rightarrow Ca^{++} + Mg(OH)_2$$
$$Ca^{++} + Na_2CO_3 \rightarrow CaCO_3 + 2Na^+$$
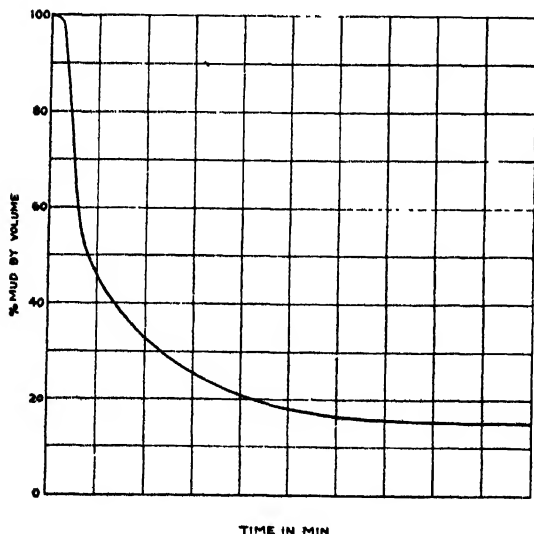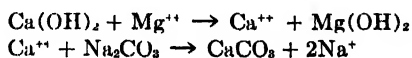
Fig. 14

Curve showing the rate of settling of mud.

Thus, sodium salts are formed instead of ammonium salts in amounts equivalent to the calcium and magnesium salts originally present, and these sodium salts will form sodium bicarbonate in the columns in the same way as sodium chloride, giving better decomposition. However, this pretreatment must necessarily be done in the cold, because the brine so treated has to be used in various washers to scrub spent ammonia gases, on its way to the absorber. There will be certain difficulty in settling

the mud from the cold brine. When, however, the process is adequately controlled, the magnesium and calcium precipitates form a reasonably quick settling "floc" (probably also as a double salt), even in cold concentrated brine whose viscosity during winter operations amounts to 3 centipoises. Therefore, given a properly designed settler, a clear brine with a highly concentrated sludge can be obtained. For this purpose, a Spaulding type of "precipitator," or reaction-thickener (see Fig. 107, p. 385), is most suitable. It is interesting to observe that, as long as sufficient lime is present in the brine (but not too large an excess), the rate of settling is quite rapid even in cold brine. A characteristic settling curve is shown in Fig. 14. Also, when a sufficient quantity of lime (equal to, or in slight excess of, the equivalents of magnesium present) is so employed, the removal of magnesium from the brine can be as high as **97-99** per cent. Table 28 shows the composition of brine before and after treatment.

TABLE 28. Composition of Raw and Purified Brine.

	Analytical Results (grams per liter)			Conventional Combination (grams per liter)	
	Raw Brine	Purified Brine		Raw Brine	Purified Brine
Cl^-	183.0	182.0	$NaCl$	300.4	302.0
Na^+	117.5	120.4	$CaSO_4$	4.81	....
SO_4^{--}	3.4	3.4	$CaCl_2$	0.80	0.011
Ca^{++}	1.7	0.004	$MgCl_2$	0.35	0.012
Mg^{++}	0.09	0.003	Na_2SO_4	....	5.03
Turbidity	clear	5-7 p.p.m.			

This method of purification requires a slight excess of lime and soda ash, and the finished brine has a pH value of 9.0. The lime used is best in the form of milk of lime or hydrated powder, because quicklime often contains overburnt or underburnt pieces which do not dissolve readily in brine. The slight dilution in the purified brine shown above is due to water added in the milk of lime used. On the other hand, the gain in Na is due to the soda ash added. In rock-salt brine, the magnesium present is sometimes negligible, so that lime may be omitted. A small amount of brine is lost in purging the mud from the pretreatment system, but with proper thickener design, this loss is seldom over 1 per cent. This is indeed negligible in view of the fact that the utilization of brine in the process itself is not more than **72-73** per cent.

This method is advantageous because there is no ammonia loss involved and all calcium and magnesium salts are converted to the corresponding sodium salts available for ammonia soda production. However, it involves the consumption of soda ash.

(4) **Treatment with lime and sodium sulfate.** The underlying principle in this treatment is first to precipitate magnesium with lime, as mentioned before, and then to precipitate most of the calcium as $CaSO_4$ by the addition of sodium sulfate. Thus, sodium sulfate is substituted for soda ash, but it does not completely throw down all the calcium, especially in the cold condition. Using a large excess of sodium sulfate—50 per cent or more of the theoretical quantity—we may eliminate under good

conditions 85-90 per cent of the total calcium present in solution after lime has been added for the precipitation of magnesium in the raw brine. But the reaction is preferably carried out in the warm condition, and at least two hours' settling time must be allowed for coagulation.

The much larger quantity of sodium sulfate required may appear, at the first thought, to be uneconomical; but if a crude sodium sulfate bittern with high salt content is available, this cheap material may be utilized for this treatment. The use of excess sodium sulfate does no harm, as sodium in the form of sulfate or chloride is equally available for the production of sodium bicarbonate in the columns. On the other hand, no ammonium salts are formed, as would be the case if ammonia and carbon dioxide gas were used. The last portion of calcium left in the treated brine may be thrown out with a small amount of soda ash, or it may be taken care of in the settling vats in the process of ammoniation.

Reference has already been made to the objection to the presence of ammonium salts in ammoniated brine, especially when sea brine is used, when ammonia and carbon dioxide gas (ammonium carbonate) are employed for the treatment. In the tower operation, the decomposition of sodium bicarbonate yields ammonium chloride, as shown in the following reaction:

$$NaCl + NH_4HCO_3 \rightleftharpoons NaHCO_3 + NH_4Cl.$$

It is to be expected that the presence of ammonium salts in the ammoniated brine (*i.e.*, the presence of fixed ammonia) will shift the equilibrium point to the left of the equation, suppressing the reaction. Indeed, when fixed ammonia is present in excess of 35 g (as NH_4Cl) per liter of the ammoniated brine, the reaction is noticeably affected, and the decomposition of sodium chloride is lowered. This corresponds to about 0.65 equivalent of the combined calcium and magnesium salts per liter of the raw brine. In terms of sodium chloride concentration in the ammoniated brine, this represents 14.5-15.0 per cent of NaCl. Normally, in rock-salt brine, the combined calcium and magnesium salts are present to the extent of 0.045-0.050 equivalent per liter (about 70-80 per cent Ca, 20-30 per cent Mg), and in sea salt they are 0.050-0.055 equivalent per liter (about 30-40 per cent Ca, 60-70 per cent Mg). This is much below the limit at which the corresponding ammonium salts begin to affect the tower reaction. But when we consider the use of sea brine (which is simply brought to saturation by solar evaporation) the combined calcium and magnesium salts then are present to the extent of 0.75-0.80 equivalent per liter (about 10-20 per cent Ca, 80-90 per cent Mg). This indeed exceeds the limit mentioned above and would cut down the decomposition of NaCl in the columns by 5-7 per cent. This difficulty is aggravated because of the much larger proportion of magnesium present in the impurities. The extent to which decomposition is lowered depends upon the amount of fixed ammonia present. Hence, in the case of sea brine containing impurities beyond 0.65 equivalent of the combined calcium and magnesium salts per liter, it is preferable to use sodium carbonate instead of

ammonium carbonate, *i.e.*, ammonia and carbon dioxide gas, for the precipitation of calcium. However, as discussed in Chapter XXVII, when ammonium chloride is to be recovered from the mother liquor which is to be made up and sent back to the columns, the treatment with ammonia and carbon dioxide gas entails no such disadvantages.

Chapter VI

Burning of Limestone

GENERAL AND THEORETICAL

Lime burning is one of the oldest industries carried on by mankind. From ancient times, lime has been used as a building material, although the chemistry underlying the process was not understood until the time of Lavoisier. Lime burning consists in driving out carbon dioxide gas from limestone by heat. This occurs at a comparatively high temperature, because the decomposition absorbs heat. The amount of heat absorbed per gram mol of limestone decomposed is 42,900 calories at room temperature or 38,500* cal. at the temperature of decomposition. The former is the heat effect for the process starting and ending at 15° C. and at constant pressure. The thermo-chemical equation is:

$$CaCO_3 \rightarrow CaO + CO_2 - 42,900 \text{ cal.}$$
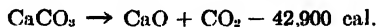
The minus sign before 42,900 cal. shows that this amount of heat is absorbed per g-mol of limestone during decomposition at room temperature. The heat is supplied by the burning of some fuel, generally coke. Anthracite is sometimes used in the lime kilns in the ammonia soda industry, but there would be more impurities in the gas.

There is a definite vapor pressure of carbon dioxide gas from limestone at a given temperature, just as there is a definite aqueous tension above water at a given temperature. Like aqueous tension, too, this vapor pressure of carbon dioxide increases very rapidly with the temperature. Like the system of water with its vapor, this system, $CaCO_3$—CaO—CO_2, is a mono-variant one, there being two independent components, CaO and CO_2, and three phases, two solid phases, $CaCO_3$ and CaO, and one gaseous phase, CO_2. Hence there is only one degree of freedom.

The equilibrium of the reaction, $CaCO_3 \rightarrow CaO + CO_2$, gives
(solid)   (solid)   (gas)

$$\frac{C_{CO_2} \times C_{CaO}}{C_{CaCO_3}} = K_1;$$

where C_{CO_2}, C_{CaO}, and C_{CaCO_3} are molal concentrations of the respective components, but both C_{CaO} and C_{CaCO_3} are constant, being present in solid form.

$$\therefore C_{CO_2} = K_C, \text{ or } P_{CO_2} = K_P;$$

* J. Johnston, The Thermal Dissociation of $CaCO_3$, J. Am. Chem. Soc., 938 (1910)

TABLE 29. Vapor Pressure of CO_2 in Equilibrium with Calcium Carbonate.

Temperature (° C.)	Vapor Pressure of CO_2 (Mm. Hg)	Temperature (° C.)	Vapor Pressure of CO_2 (Mm. Hg)
587	1.0	749	72
605	2.3	777	105
631	4.0	786	134
671	13.5	795	150
673	14.5	800	183
680	15.8	819	235
682	16.7	830	255
691	19.0	840	311
701	23.0	852	381
703	25.5	857	420
711	32.7	871	537
727	44	881	603
736	54	891	684
743	60	894	716
748	70	898 *	760

* Figure obtained by Johnston by extrapolation.

where C_{CO_2} is the molal concentration and P_{CO_2} is the vapor pressure of CO_2 gas.

Table 29 shows the vapor pressure of carbon dioxide from calcium carbonate at a given temperature according to the investigation by Johnston.*

From $P_{CO_2} = K_p$ above, by the van't Hoff equation, we have

$$\frac{d \ln K_P}{dT} = \frac{\Delta H}{RT^2}$$

where ΔH is positive when the heat is absorbed. It is seen that K_p increases, *i.e.*, the partial pressure of carbon dioxide in equilibrium with the limestone increases as the temperature is raised.

Since K_p is numerically equal to the partial pressure of carbon dioxide, with two sets of temperatures and the corresponding partial pressures of carbon dioxide, it should be possible to calculate the theoretical heat of decomposition of calcium carbonate. If we accept Johnston's figures, *i.e.*, at 891° C. $P_{CO_2} = 684$ mm., and at 894° C. $P_{CO_2} = 716$ mm., we may calculate the heat of decomposition as follows. Within the range of 3° C. we may assume that ΔH is constant, and the expression after integration between the limits 891 and 894° C. is shown below.

$$\log \frac{716}{684} = \frac{\Delta H}{2.303 \times 1.99}\left(\frac{1}{1164} - \frac{1}{1167}\right)$$

whence

$$\Delta H = \frac{.0198 \times 2.303 \times 1.99 \times 1164 \times 1167}{1167 - 1164}$$
$$= 41,000 \text{ Cals. per mol of } CaCO_3$$

Although theoretically a temperature of 898° C. is sufficient to decompose limestone with a vapor pressure of CO_2 of one atmosphere, the rate

* J. Johnston, The Thermal Dissociation of $CaCO_3$, *J. Am. Chem. Soc.*, 938 (1910).

of dissociation is slow; thus, in practice, the temperature in a lime kiln is considerably above 900° C. C. C. Furnas [*] in his study of the rate of calcination gave the relationship between the temperature at which calcination takes place and the duration of time required as shown in Fig. 15. Calcination temperature is generally taken to be 940° C., while the temperature at the decomposition zone is more nearly 1050° C. under kiln conditions. Sometimes the temperature rises as high as 1200° C. When the lime is allowed to remain for a few hours at this high temperature, it is changed to a denser mass, showing a dark, grayish, or yellowish tinge
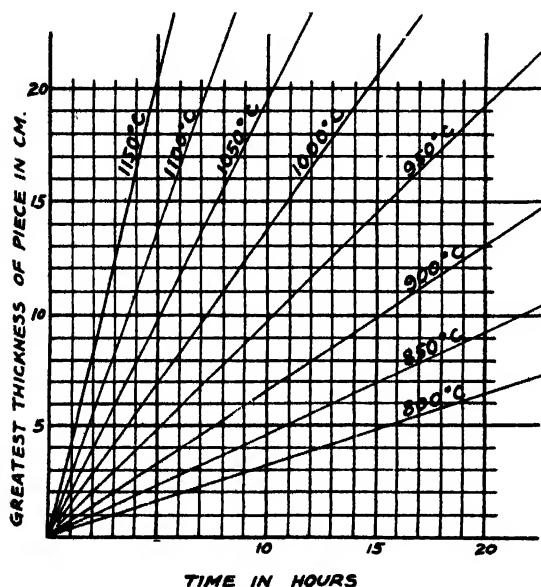
FIG. 15.

Relation between time required for calcination, temperature, and thickness of piece (Furnas data).

with minute checks. This dense lime presents less surface and requires a much longer time for solution, and the particles suspended in the milk of lime react more slowly with the ammonium chloride solution. Such lime is called overburnt or dead-burnt lime. Besides giving difficulties as the result of its slow reaction in the prelimer and lime still, it may cause difficulties by lowering the settling rate in the causticizing operation. Properly burnt lime is practically cream-white and is readily hydrated to a loose, pure-white powder. Hence the name "fat lime."

Lime is a comparatively active base. It is sometimes called quicklime or caustic lime. Hydrating consists in converting the oxide to hydroxide by adding just enough water to the lump when the mass disintegrates and turns white, but does not become pasty or wet. Considerable heat is involved during hydrating or slaking. The following thermochemical equation shows the heat effect.

[*] Furnas, C. C., The Rate of Calcination of Limestone, *Ind. Eng. Chem.*, **23**, 534 (1931).
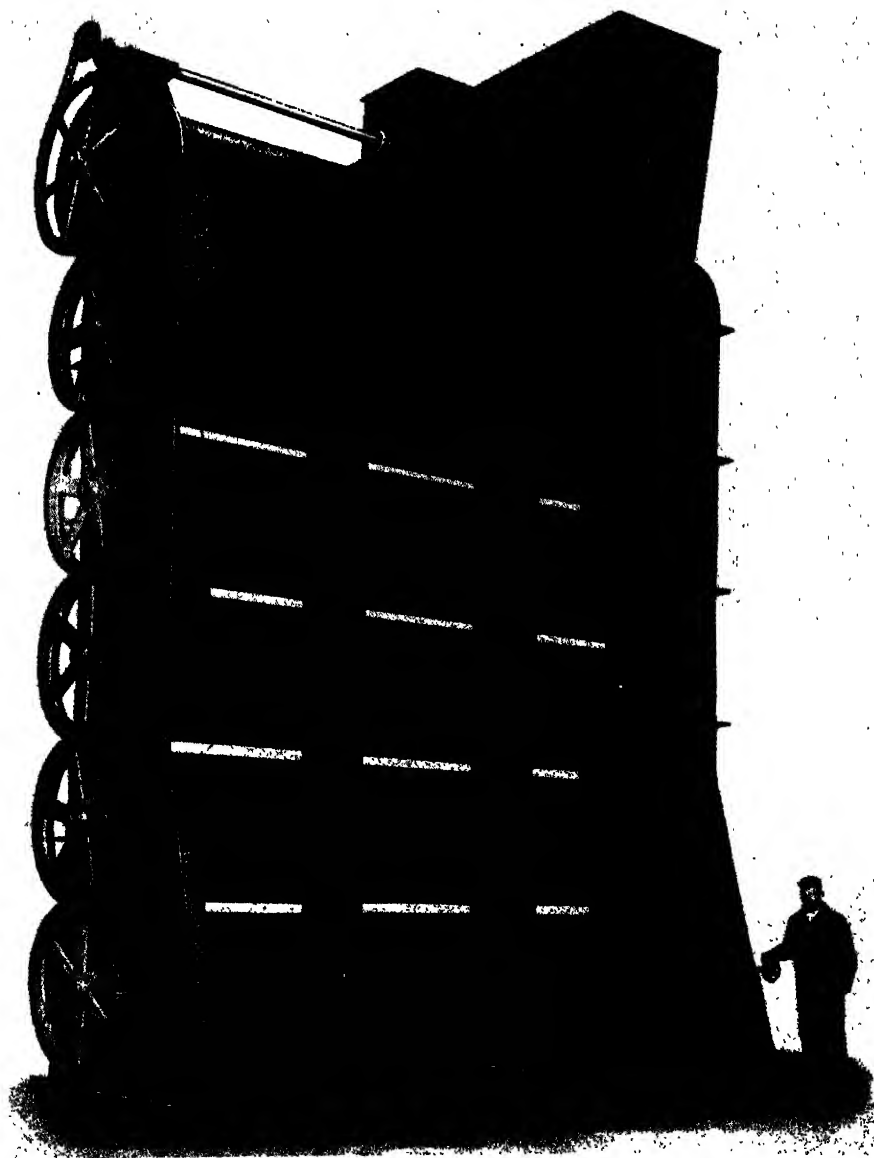
Courtesy The Kritzer Co.

Fɪɢ. 16. Kritzer continuous cylindrical hydrator.

$$CaO + H_2O \rightarrow Ca(OH)_2 + 15{,}540 \text{ cal. (Thomsen)}$$
(solid) (liquid)   (solid)
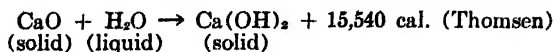
The plus sign shows that the heat is evolved when quicklime absorbs water in slaking. During hydrating the lump disintegrates to a fine powder leaving unburnt stone in a lump form. This is a good way to separate lime from the unburnt core.
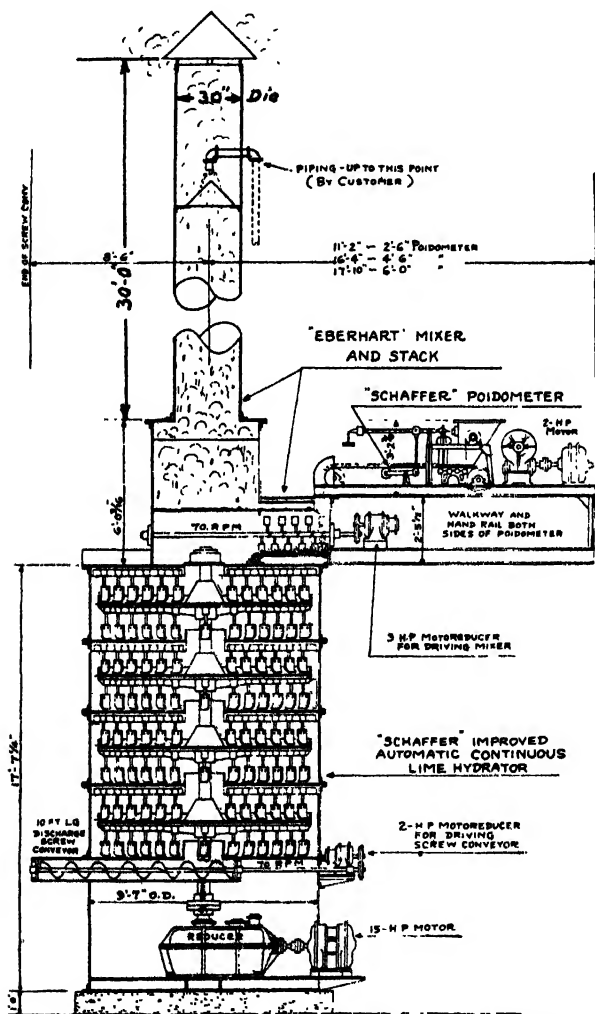
Courtesy Mr. L. H. Eberhart

FIG. 17. The Schaffer continuous hydrator.

Hydrated lime has become a favored form in which lime is handled in commerce. Various types of machines called hydrators have been designed for hydrating the lump lime. They consist of either a vertical

shelf construction, such as the Schaffer continuous hydrator, or of sections of stationary cylinders, one on top of another, with a rotating screw ribbon in each cylinder, such as the Kritzer continuous hydrator. Lumps of lime are charged into the top and a small excess of water over the theoretical quantity necessary to form $Ca(OH)_2$ is sprinkled over them. The stirring action helps to distribute the water and scrape the lime along. In the Kritzer type (Fig. 16) a number of cylinders one on top of another, work the lime down in a zigzag way, taking the lime from a small pre-hydrator on the top into which water is sprinkled and discharging the hydrated lime from the bottom cylinder, much in the same way as the Hasenclever mechanical chambers for the bleaching powder manufacture (see Chapter XX under "Manufacture of Bleaching Powder"). The Schaffer machine (Fig. 17) consists of a number of shelves placed one on top of the other with revolving rabbles arranged much in the same manner as in the Herreshoff roaster. The hydrated lime is then screened to separate out unburned cores. Hydrated lime has many advantages over lump lime. It is purer and more uniform, does not burn the bags if they should get wet during transportation, does not readily become "air-slaked," and has the advantage of being "aged." Quicklime (CaO), on exposure to air, absorbs carbon dioxide from the air and reverts to calcium carbonate. Such lime is termed "air-slaked;" for the reaction is a reversible one:

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

At ordinary temperature, the partial vapor pressure of carbon dioxide in equilibrium with calcium carbonate is so very small (only 1 mm. at 587° C. and 23 mm. at 701° C.) that the small amount of carbon dioxide gas in the air is sufficient to set up equilibrium and convert calcium oxide (lime) back to calcium carbonate.

Lime (CaO) is very slightly soluble in water, its solubility product being 0.64×10^{-5} at 20° C. (Shipley and McHaffie). In grams per liter, its solubility is given by Guthrie in Table 30:

TABLE 30. Solubility of Lime.

Temperature (° C.)	CaO (Grams per liter)	Temperature (° C.)	CaO (Grams per liter)
5	1.350	50	0.981
10	1.342	60	0.879
15	1.320	70	0.781
20	1.293	80	0.741
30	1.219	90	0.696
40	1.119	100	0.597

An interesting fact is that its solubility decreases as the temperature is raised.

Lime is so sparingly soluble that its solution would be too dilute for general purposes. Therefore it is introduced usually in the form of a suspension called milk of lime. In milk of lime there is an equilibrium between the solid lime and the lime that has gone into solution, small as

it is.   And what is dissolved is again in equilibrium with the calcium and hydroxyl ions in solution.   Thus,

$$\text{Ca(OH)}_2 \qquad \text{Ca(OH)}_2 \qquad \text{Ca}^{++} + 2\text{OH}^-$$
$$\text{(solid)} \qquad \text{(diss.)}$$
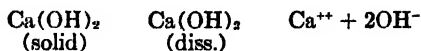
As the reaction goes on (*i.e.*, say as the OH^- ions are used up) more Ca(OH)_2 (diss.) must dissociate and more Ca(OH)_2 (solid) must dissolve.   Hence all solid particles of Ca(OH)_2 in the lime suspension are thus readily available for reaction.   Table 31 shows that milk of lime of different concentrations has the following specific gravity given by Lunge.

TABLE 31.   Specific Gravity of Milk of Lime.

Sp. Gr. at 15° C.	CaO (Grams per liter)	Sp. Gr. at 15° C.	CaO (Grams per liter)
1.01	11.7	1.14	177
1.02	24.4	1.15	190
1.03	37.1	1.16	203
1.04	49.8	1.17	216
1.05	62.5	1.18	229
1.06	75.2	1.19	242
1.07	87.9	1.20	255
1.08	100	1.21	268
1.09	113	1.22	281
1.10	126	1.23	294
1.11	138	1.24	307
1.12	152	1.25	321
1.13	164		

With lime containing as impurities considerable quantities of sand, clay, finely divided unburnt stone (CaCO_3), etc., the apparent specific gravity of the milk of lime is always greater and its determination furnishes only a very rough guide.   Milk of lime from a poor grade of limestone may have a specific gravity of 1.3 and yet contain not more than 200 grams of CaO per liter.

Limestone is frequently found to contain magnesium carbonate, varying from 45 per cent in the case of dolomite, $\text{CaMg(CO}_3)_2$, to but a fraction of 1 per cent in a high-grade limestone   A large percentage of MgCO_3 in the limestone is rather objectionable for its inertness in the distillation of ammonia.   It may be remarked here that the presence of magnesium in lime is, as a rule, undesirable.   One can think of the objection to magnesia in the cement industry, in the bisulfite process in the paper industry, in the calcium carbide process in the air nitrogen industry, in the manufacture of bleaching powder, and in the lime mortar and lime plaster (as "lean lime").   For furnishing CO_2 gas in the ammonia soda industry, however, MgCO_3 in limestone serves equally well, and in fact, carbon dioxide gas from MgCO_3 is driven off with greater ease; but for ammonia distillation, magnesia in the lime is entirely unavailable.   The thermochemical equation is

$$\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2 - 28{,}900 \text{ cal. (de Forcrand)}$$
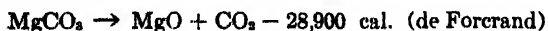
The minus sign again shows the heat absorbed during decomposition per mol $MgCO_3$. Table 32 gives data on the vapor pressure of carbon dioxide from $MgCO_3$ (native magnesite) by Mitchell.[*]

TABLE 32. Vapor Pressure of		from Native Magnesite.	
Temperature (° C.)	Vapor Pressure of CO_2 (Mm. Hg)	Temperature (° C.)	Vapor Pressure of CO_2 (Mm. Hg)
447	10.5	567	23.0
457	11.0	587	27.5
467	11.6	597	31.3
487	12.9	607	34.6
497	13.7	637	39.6
507	14.6	677	61.2
517	15.5	707	117
527	16.6	727	316.5
537	18.1	747	602.5
547	19.5	756	760
557	21.1		

The heat of decomposition of $MgCO_3$ is only 28,900 cal. while that for $CaCO_3$ is 42,900 cal. (room temperature) and the decomposition temperature for $MgCO_3$ is 756° C. as against 898° C. for $CaCO_3$. The smaller quantity of molal heat absorbed and the lower calcination temperature show greater ease of decomposition of $MgCO_3$ in comparison with $CaCO_3$.

The objection to MgO for ammonia distillation is not that it will not react with NH_4Cl and $(NH_4)_2SO_4$ to free NH_3, but that its reaction is slow and must be carried out under special conditions. Under certain conditions the following reaction does occur:

$$Mg(OH)_2 + 2NH_4Cl \rightarrow MgCl_2 + 2NH_4OH$$

As a matter of fact, MgO has been proposed for ammonia distillation in soda works, because it is considered possible to recover by-products of $MgCl_2$ from the distiller waste in the form of chlorine, Mg_2OCl_2, HCl, etc. Under ordinary conditions, however, all the MgO passes through the distiller unreacted upon, and only CaO is utilized. The solubility product of $Mg(OH)_2$ is only 1.2×10^{-11} at 18° C. (Johnston) as against 0.64×10^{-5} for CaO at 20° C. The heat of hydration of MgO, too, is less.

$$MgO + H_2O - Mg(OH)_2 + 5,000 \text{ Cal. (Marignac)}$$
$$\text{(solid) (liquid)} \quad \text{(solid)}$$
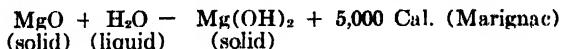
The corersponding heat of hydration for CaO is 15,540 cal.

Furnas (*loc. cit.*), in his study of the calcination of limestone, differentiates the rate of calcination and the rate of heat penetration (temperature wave). By the rate of calcination is meant the rate of advance of the line of calcination from the outside toward the center of the stone, which is dependent on the heat conductivity of the limestone; and by the rate of heat penetration is meant the rate of advance of temperature wave. It is found that decomposition (calcination) in the center of the

[*] Mitchell, A. E., *J. Chem. Soc. (London), Trans.*, Part I, **123**, 1055.

stone may not take place, even if the calcination temperature has been reached there. The center portion is then in a meta-stable state. According to Furnas, the rate of calcination (R) is a logarithmic function with respect to the temperature (t). Thus,

$$\log R = 0.003145t - 3.3085$$

where R = rate of advance of line of calcination in cm. per hour, and
            t = temperature in ° C

This equation is fitted to the curve shown in Fig. 18.
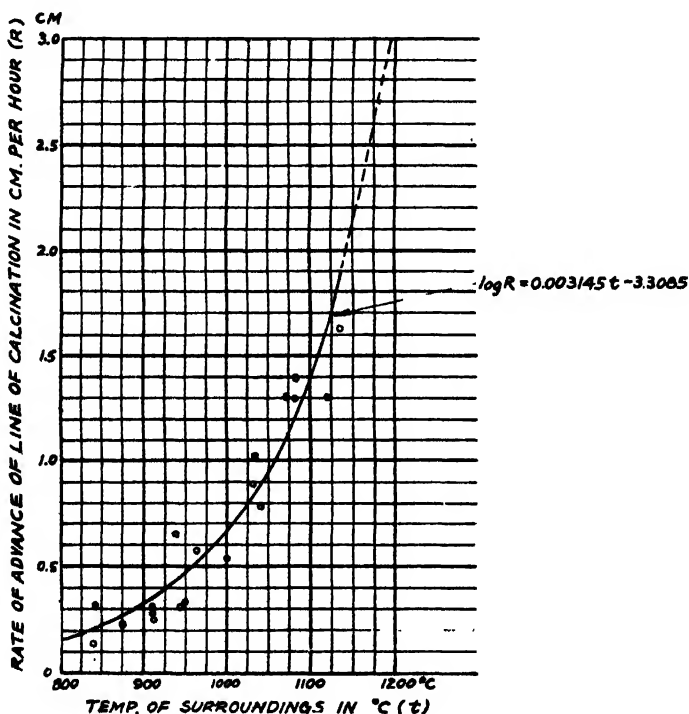
Fig. 18.   Rate of advance of line of calcination vs. temperature of surroundings (Furnas data).

Unfortunately, Furnas' study covered only the size range between 2.5 cm. (1″) and 8.5 cm. (3⅜″), but he stated that it might hold up to 15-20 cm. (6″-8″). It is thus seen that the length of time required for complete calcination is directly proportional to the size (diameter) of the stone (as expected), other conditions being equal. In each individual piece of the stone, the calcination zone or boundary is very sharp and the temperature travels faster than the line of calcination, so that even though the center portion might have attained the temperature of the outside surroundings, decomposition lags behind. Decomposition of limestone, like the boiling of water, is marked by a definite temperature which

remains constant until the process is complete, after which the temperature begins to rise to approach the outside temperature. The rate of advance of the line of calcination may slightly decrease as calcination progresses, because of the longer path through the calcined zone, over which heat for calcination must travel.

Based on the above, the rate of CO_2 gas evolution may be estimated for a given piece of high-quality limestone, as follows:

Let

V = volume of CO_2 gas evolved, in liters (N.T.P.).
D = diameter of a given piece of limestone in cm.
θ = time in hours.
ρ = density of the stone in grams per ccm.
p = per cent of $CaCO_3$ in the stone.

Then $\dfrac{dV}{d\theta}$ = the volume-rate of the CO_2 per unit time (liters per hour).

The rate of the advance of the boundary line is R radially. The depth of calcination boundary (of line of calcination from the surface) is $R\theta$ at any given instant. Consider a spherical form. The diameter of the spherical boundary then is $D - 2R\theta$, and the spherical surface of the boundary is $\pi(D - 2R\theta)^2$. The molecular weight of $CaCO_3$ is 100 and the G.M.V. is 22.4 liters.

Therefore, $\dfrac{dV}{d\theta} = \pi(D - 2R\theta)^2 R\rho p \times \dfrac{22.4}{100}$

$= 1.83\, pR\,(D - 2R\theta)^2$ (the density ρ is 2.6 for average limestone)

That is, $V = 1.83\, p \displaystyle\int_0^\theta R\,(D - 2R\theta)^2\, d\theta$

The rate of advance of calcination inward depends upon the temperature only and is specific for a given grade of limestone, *i.e.*, R is independent of θ as a first approximation. Integrating, we obtain,

$$V = 1.83\, pR\theta\left(D^2 - 2RD\theta + \frac{4R^2\theta^2}{3}\right)$$

At 1052° C., which is near the average temperature of calcination in kiln practice, R is very nearly one cm. per hour on the average for a high-grade limestone (about 97 per cent $CaCO_3$ and 2-2½ per cent $MgCO_3$).

Therefore, $V = 0.61\, p\theta\,(3D^2 - 6D\theta + 4\theta^2)$

The above equation holds true only for a high-grade limestone, because it has not taken into consideration CO_2 that comes from the small quantity of $MgCO_3$ present. Further, it is based on the assumption that the rate of calcination is constant and is approximately 1 cm. per hour at a temperature of calcination of 1052° C. This rate of calcination would be considerably above 1 cm. when there is a higher percentage of magnesium carbonate present in the limestone, due to the greater ease with which $MgCO_3$ is calcined (decomposed) compared with $CaCO_3$.

Quarrying of Limestone and Preparation of the Charge

Limestone is generally quarried by open pit methods. Unless the over-burden is thick, mining is seldom resorted to. Often the surface soil is just stripped off and open stope is employed. But where the top soil is extensive and thick, or where the upper layers consist of a high silica or alumina limestone (such as the cement rock frequently encountered), tunnelling from the sides into lower levels, where there is a high quality limestone, is a common practice. In such cases quarry cars are usually run on rails into the tunnels at a slight grade. As a rule, pumping to keep the pits dry is a very essential operation as in all mining stopes, if there is much underground water.

Details of quarrying depend upon the physical characteristics of the rock, its composition, its bedding angle, and the amount of over-burden. Where the formation permits, deep faces from 30 to 125 feet are employed, but where the bedding is flat, the face may be in any position, governed by the convenience in the transportation of the stone. If the beds are steep and almost vertical, the face should best be at right angles to the strike of the beds rather than parallel to it. Blasting of the rock then should start from the bottom of the face, as it is easier to remove the stone from the bottom. Dynamite is usually used for blasting. Dynamite sticks are 8 inches long, but may be $\frac{7}{8}$, 1, 1$\frac{1}{8}$, 1$\frac{1}{4}$, etc. in. up to 4 or 5 inches in diameter. The 1$\frac{1}{4}$-inch size is the commonest. Each of the 1$\frac{1}{4}$- by 8-inch sticks weighs about $\frac{1}{2}$ lb. and a large number of these sticks are generally placed in one hole, one above the other. For a limestone quarry, it is generally figured that on the average 3 to 4 tons of stone are blasted per lb. of dynamite charge.

Blasting is done by drilling the rock with jackhammers, generally of 55-lb. weight with 1-inch hexagonal hollow drill rods. These jackhammers require 80-90 lbs. of air pressure, and each requires for operation 90-110 cubic feet of free air per minute, depending upon the air pressure. Usually one man works on each jackhammer of this size. The drill bits may be detachable or integral with the drill rods. Detachable bits may be re-ground three or four times before they are worn and discarded. Integral bits may be clamped, shaped, formed and sharpened from the drill rods in suitable die blocks and dollies and the center holes punched, using a drill sharpener (also driven by compressed air), until the steel stock is used up. The bits may be 1$\frac{1}{2}$, 1$\frac{3}{8}$ and 1$\frac{1}{4}$ or 1$\frac{3}{8}$, 1$\frac{1}{4}$ and 1$\frac{1}{8}$ inches in diameter respectively. The holes are drilled to 12 to 16 feet, in steps, using 1-inch hexagonal drill rods. The holes are drilled in rows at a distance of 5 to 6 feet between centers. They may be drilled horizontally or vertically, depending on the position of the face or ledge. Drilling may be done dry, or wet, or dry with vacuum suction using a dust separator (such as in the "Drill-vac" outfit). Simple dry drilling is not to be recommended as it creates too much dust in closed space for the health of the workmen. Where the rock is silicious, laws are quite strict in prescribing the dust limits to protect workmen against silicosis.

For large-scale quarrying operations, holes as large as 6 inches in diameter are drilled into the rock, and may be as deep as 125 feet, or about 5 feet below the floor of the face. These holes are drilled about 20 feet from the edge and are spaced at 20 foot centers in rows about 20 feet apart. Dynamite blasting is done by special workers. These larger holes at a greater distance apart are used for economy of labor.

When tunnelling is required, the tunnels may be from 35 to 50 feet wide by about 40 feet high. "Pillars" are left between tunnels or "drifts" for roof support. The width (or diameter) of these pillars varies from the width of the tunnel to 1½ times the width, and the roof of the tunnel may be flat or arched, depending upon the strength of the rock. As a rule, timbering is seldom necessary. Shafts or "raises" are located at high places at the back of these tunnels for the purpose of ventilation. Except in extreme cases, a couple of these raises, suitably located, suffice for natural draft ventilation, and no mine fan or exhauster is necessary.

Blasting in tunnels is done by drilling holes first at the top horizontally into the face and blasting off the top portion to form a bench. Then the holes are drilled vertically into the ledge at a proper distance from the face. Generally these holes are drilled in rows and spaced 5-6 feet apart, and about 8 feet from the face. Dynamite is loaded into the holes and fuses are put in with varying lengths increasing by about 6 inches from the center to each of successive holes toward the side, so that when electrical contact is made the powder is set off first in the center holes and then in the other holes a few seconds apart from the center outward.

Frequently in larger quarries a heavier drill mounted on a portable carriage and suspended on a chain from a small mast is employed. Such drills are then operated by two men to each drill and have maximum maneuverability. The carriage may be anchored in any position and the drill adapted to different locations. Deep holes may be drilled this way.

The stone is removed by steam shovels and loaded directly into cars on a track or into trucks, which haul it into the crushing and screening plant.

One source of serious trouble in quarry tunnels is the spalling or peeling off of the ceiling in the tunnels, especially when the ceiling is a layer of shale. This is found to be caused by the humid conditions in the tunnels (sweating during summer days), fluctuations of temperatures, and general weathering. Falling more likely occurs near the entrances or at places exposed to outside atmosphere. Such falling of pieces from the ceiling is a menace, endangers human lives, and interferes with the quarry operation. Often, painting the ceiling with a waterproof coal-tar paint such as "EBONOL" made by Sherwin Williams Company will prevent or minimize the trouble. This may be applied by a spray gun. Sometimes, Gunite is a great help, and if properly applied, will give an impervious coating and add strength to the ceiling. The Gunite should not be less than an inch thick and may be applied in two layers, the first or

bottom layer being only $\frac{1}{4}$ inch thick and the top over $\frac{3}{4}$ inch thick. Limestone surface is less liable to peel off this way. If the shale ceiling is thin with another layer of limestone just above it, it is best to take the whole shale roof down, leaving the limestone surface exposed, which will be more permanent.

Ammonia soda manufacturers sometimes have to quarry and haul limestone over a long distance, either by rail or in river barges. Certain alkali plants are not so fortunately situated as to have both limestone and salt close at hand. It is often a debatable question whether an ammonia soda plant should be located near the source of limestone supply or near the source of salt supply, if no good limestone is found near the locality where salt is available. One of the plants on Lake Erie in the United States has to ship limestone by water from the coast of Michigan. One of the recently established alkali plants in the South has to transport limestone for a considerable distance. An alkali plant in North China hauls its limestone to the plant site over a distance of from 56 to 90 miles by rail, and occasionally also by coastal boats over 200 miles across the sea. Limestone is one of the two most important raw materials used in ammonia soda manufacture, and only a good grade should be used for economical operation.

Limestone for ammonia soda operation is generally quarried under the supervision of the soda ash plant management. Almost invariably some sort of over-burden must be removed and the main kiln supply must be blasted, crushed, screened, (washed if necessary), and stored away preparatory to feeding the kiln. The most common procedure is to transport the stone from the quarry to the plant after all crushing, screening and washing operations have been completed. Occasionally, because of lack of water or other facilities at the quarry, the screening and washing operations are conducted near the plant.

Often two strata of stone are worked at the same time, and these have different composition as regards impurities and physical characteristics. This may necessitate proper mixing and proportioning to obtain best results. If the variations in mixture do not involve any deep-seated effect on kiln operations, accurate control in the blending is, of course, unnecessary.

Since the stone for any one kiln should be as uniform in size as possible, screening operations are conducted at the quarry to give certain cuts or screen sizes of stone. The larger sizes in common use are about 6 inches in diameter. The range of sizes generally permits a ratio of two-to-one or even three-to-one variation. If a quarry is operated for a plant having only one lime kiln in operation, everything below the minimum allowable limit must be rejected and sold for other purposes, such as railroad track ballast, road building, concrete aggregate, etc. If there are several kilns in operation at the plant, one of them may be kept operating on the smaller sizes of stone which result from the crushing and screening operations. This is quite feasible, provided the latter are reasonably uniform in size. The smaller size simply requires some-

what greater blast pressure for its burning. Vertical kilns very seldom use any pieces smaller than 2 inches, but the small pieces of fines are occasionally brought to the plant and burned in rotary kilns.

The type of crushing equipment depends on the size of the quarry. The largest plants will place the quarrying "shots" so as to produce relatively large pieces. Quarrying shovels, cars, etc. are then all proportionately large and all the quarrying product is put through a huge primary crusher, sometimes capable of taking a piece 4-5 feet in the maximum dimension. In smaller quarries this entire line of equipment is scaled down, requiring closer spacing of blast holes and a larger number of "pot shots" for reducing the size of individual pieces shot down from the quarry face. In some plants the preliminary crusher is of the gyratory type; in others the jaw type is used. From the preliminary crusher the product is given a size separation, the over-size pieces being returned to the crusher for further reduction. This is one example of closed-circuit operation. From here on, secondary crushers and screens prepare the various grades of stone most suitable to the particular operation.

Many quarries have an over-burden such that it may introduce an objectionable quantity of clay or silicious matter which would obstruct the passages in the kiln by the formation of low-melting clinkers. Washing operations may be necessary under these conditions, and more or less standardized washing equipment is used.

The stone is transported from the quarry or washing plant to the kiln site by rail, by water, in narrow- or standard-gage cars, on cableway systems, or occasionally by direct conveyors when the two are close enough to each other. A stock pile of kiln size stone is kept at both ends of the system to insure continuity of soda plant operation against breakdown or bad weather conditions.

Limestone is sedimentary in origin and its deposits often contain many impurities. It has many different physical characteristics and chemical compositions. Natural products range from the purest marble, calcite, aragonite, etc., to ordinary grades of limestone for industrial purposes. There are argillaceous limestone containing considerable clay; arenaceous limestone containing large amounts of silica; magnesian limestone containing 10 to 30 per cent magnesium carbonate; and dolomite containing 45.65 per cent magnesium carbonate. These argillaceous and arenaceous limestones, while very desirable for the manufacture of cement and hydraulic lime, cannot be used in the ammonia soda industry on account of their silicious content. Dolomitic or magnesian limestones are not desirable, or at least are uneconomical because of their magnesia content, although small proportions (1 to 6 per cent $MgCO_3$) can be tolerated. In general, the ammonia soda industry demands a high-grade limestone in order to have successful and economical operation. Especially is this true when the waste liquor from the distiller is to be worked for $CaCl_2$ or other by-products. Specifications are given in Table 33, although no strict line of demarcation can be drawn:

TABLE 33.   Specifications for Limestone.

	Per Cent
CaCO$_3$	90-99
SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$	0-3
MgCO$_3$	0-6

Since limestone is a natural product, its physical appearance (color, texture, hardness, etc.) is very much affected by impurities, although they may be present only in small percentages.   Its geological age of formation also has considerable bearing on its physical properties.   Samples from different deposits seldom look exactly alike.   They range in color from deep blue, light gray, and stripy white, to streaky brown.   Their texture and hardness vary from a dense flinty appearance to a loose crystalline cleavage.   Both calcite and quartz are associated with limestone and appear white.   Dull color may indicate high magnesium, and crystalline luster may be indicative of high silica content.   To an experienced eye, the general appearance of limestone will reveal much about its composition, so that high-magnesia or high-silica limestone can be distinguished by inspection with considerable accuracy.

In a quarry, close supervision is exercised in selecting the best face for working, the seam that appears undesirable by inspection being left out or blasted down for some other work.

PRACTICAL OPERATION OF LIME KILN

Although lime burning is an important industry in itself, the ammonia soda industry undoubtedly constitutes one of the biggest lime producers and consumers.   Much of the development of burning technique we owe to the alkali manufacturers.

Take for example the year 1937 * when the quantity consumed by all chemical industries other than the ammonia soda industry totalled 2,151,444 short tons, distributed as in Table 34.

TABLE 34.   Lime Consumed in Different Industries in United States (1937).

Glass Works	167,438	short tons
Metallurgy	694,814	" "
Paper Mills	447,728	" "
Sugar Refineries	21,211	" "
Tanneries	61,544	" "
Water Purification	212,213	" "
Other uses	546,496	" "
Total	2,151,444	short tons

If we include lime used in building and agricultural work, the total for the year 1937 was 3,506,439 short tons, thus:

* "Lime," Minerals Year Book, Bureau of Mines, Dept. of the Interior, Washington, D. C., 1938.

Building	948,533 short tons
Agriculture	406,462 " "
Chemical Industries other than Ammonia Soda (as above)	2,151,444 " "
Total	3,506,439 short tons

In the same year this country produced 2,205,006 short tons of ammonia soda ash and 488,807 short tons of caustic soda (by lime process).

Assuming an average figure of 1.25 tons of limestone required for the manufacture of 1 ton of ammonia soda ash, or 0.75 ton of lime as burned per ton of soda ash, the total lime consumed in the manufacture of ammonia soda ash is $0.75 \times 2,205,006$, or roughly 1,654,000 short tons. If we take roughly 0.80 tons of lime per ton of caustic made, 488,807 short tons of the caustic would require approximately 391,000 short tons of lime.

Therefore, the total quantities of lime consumed by the ammonia soda and lime caustic manufacturers for the year 1937 may be estimated at 2,045,000 short tons, and this quantity is considerably more than one-half the total quantity of lime used in all other chemical industries, in building construction, and for agricultural purposes; namely, a total of 3,506,439 short tons.

For this industry, both lime and carbon dioxide are needed, and lime kiln operation plays an important rôle in the efficiency of the ammonia soda process. Hence it is imperative that kiln operation should attain high efficiency in order to obtain rich CO_2 gas. The scientific efforts of the ammonia soda technologists have done much to develop the lime industry, although little of their work has been published.

There are several different types of lime kilns. The earliest and crudest form is a small mound built of bricks or the stone itself with a pit inside, in which limestone is burned by means of wood or coal (Fig. 19). Natural draft, of course, is employed. A good product is turned out in this type of kiln. The lime is obtained in very large lumps. However, the process is tedious and there is no way to recover the gas; also the kiln has a very small capacity and low fuel efficiency. In the ammonia soda industry, by far the commonest type is the vertical-shaft kiln, also known as the Belgian kiln. The fuel used is generally coke, although anthracite may be used in certain cases. In certain localities anthracite is considerably cheaper than coke. The gas obtained when anthracite is used as fuel has a somewhat lower test and must be thoroughly scrubbed free from sulfur dioxide and coal-tar products. The best proportion for a vertical-shaft kiln is to have the height about 6-7 times the inside diameter. To economize the heat and consequently to make the richest possible gas, the modern tendency is toward increasing the height. The lining of fire brick and common brick should be about 24 inches thick for small kilns and 36 to 48 inches for large kilns, and there should be from 3 to 6 inches of space between the steel casing outside ($\frac{3}{8}$-inch plate) and the brickwork, to be filled with sand or an insulating material

in order to cut down convection and radiation losses at the casing out-side. The modern standard vertical kiln is about 14 feet inside diameter and 80 to 90 feet high. It has a capacity of about 300 to 350 tons of stone per 24 hours. The thickness of the brick lining is as much as 48 inches. The kiln is provided with a skip hoist either inclined or ver-tical, or an inclined belt conveyor. There is a charging hopper on the top
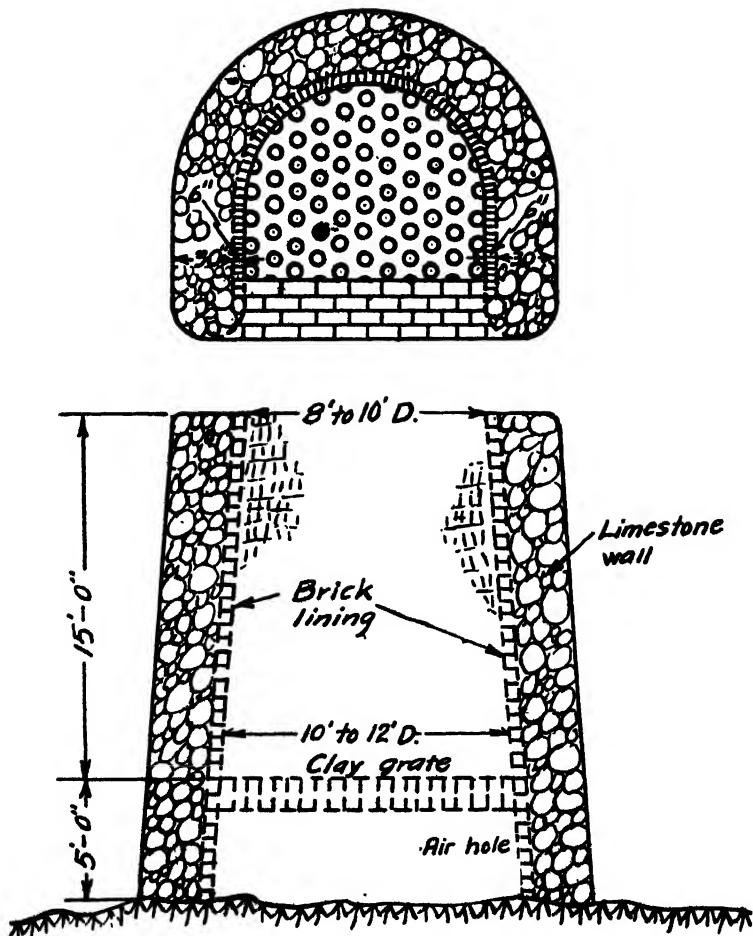
FIG. 19. Primitive lime kiln.

with one or more cones for distributing the stone and coke evenly over the entire internal area of the kiln. The entire assembly is supported on cast-iron or steel columns surrounded by a steel hood or air shield. Inside the air shield is the discharge mechanism on which the entire weight of the charge of limestone, coke and lime may be carried. The lime is drawn from the bottom by this automatic discharge mechanism.

A knife edge scrapes the lime off the revolving table. This was originally designed by Solvay and many modifications have been introduced. They operate very successfully in large units. Air is introduced through the center and through four or eight tuyeres placed at equidistant points on the circumference at the bottom of the kiln, much in the same way as in a blast furnace. The valve at each tuyere can be set to admit more or less air, as desired.

The charging hopper at the top of the kiln is provided with a heavy 45° cast-iron cone having an apron extension attached to the bottom of the hopper, consisting of four quadrants, one deflecting a portion of the charge to the center of the kiln, the next putting another portion a little farther out, the third still farther, and the fourth around the internal circumference of the kiln near the fire brick lining. The apron revolves with the hopper a quarter or a fifth of a revolution each time a charge is dumped in, thus distributing the charge evenly over the whole area in the kiln Stone and coke charged into the kiln reach the top either by means of an electrically-driven skip hoist, inclined belt conveyors, or cable ways. Proportioning of the coke with respect to stone charged may be done either by automatic-weighing scales, automatic-weighing belt sections, or feed tables, depending on the means of conveyance employed.

The discharge mechanism consists of a heavy, cast-iron spiral cone whose steps and slope are so proportioned as to take out lime from the center and the sides proportionally. The spiral cone works the lime from the center to the outside circumference. An annular table made of heavy plate steel is attached to the base of the cone and revolves with it. Lime gradually drops onto the annular table and is scraped by a stationary scraper knife, as the cone is slowly revolved. The lime scraped from the table drops onto a star feeder which feeds it into an inclined bucket elevator, carrying the lime into the bin above. The cone may be driven by a worm gear and chain sprockets. It may be mounted on twelve steel rollers running on circular cast-steel treads, forming a large roller bearing at the bottom. The lime is drawn intermittently, generally a few minutes in each 15-minute interval.

With the foregoing arrangement, both the charging of the stone and coke above, and the discharging of lime below, are very uniform and kiln operation is easily controlled. The top (gas) temperature can be maintained at as low as 40-60° C. and the bottom (lime) temperature at 40-80° C., depending on the atmospheric temperature, the rate of draw, and the distance of the fire zone from the bottom of the kiln. The kiln gas test can be maintained at an average of 42.0 per cent CO_2 for 24 hours a day, with lime uniformly and properly burned. Little overburnt lime or unburnt core is found in the draw.

The top and bottom temperatures of the kiln vary considerably according to the height of the kiln, the arrangement for lime draw, the blast pressure, and the rate of operation. With an automatic discharge mechanism (mechanical discharge), it is quite normal to obtain a top

temperature not exceeding 60° C. in summer and 30° C. in winter and a lime discharge temperature of 40-80° C. at the bottom. This draw temperature is mainly dependent on the blast pressure and the rate of draw. When the wind pressure at the bottom is low, or when, for some reason, the blast has been shut off, the fire stays low and the temperature of the lime drawn would be higher. On the other hand, when for some reason lime has not been drawn out for some time, the fire zone will creep up and the lime drawn will be colder.

Recently rotary kilns have been adapted to lime burning, but the size of the stone burned is limited to $\frac{1}{2}$ to $1\frac{1}{2}$ inches, and the lime produced is fine. For making hydrated lime, this product is not objectionable. The rotary kiln is especially suited for burning fines from the crushing plant, or calcium carbonate mud from the causticizing process. The fuel used is oil, powdered coal or producer gas. A waste heat boiler can be installed at the gas exit end to recover the heat. Due to the larger radiating surface and impracticability of extensive heat insulation or heat regeneration, the fuel efficiency of the rotary kiln is much lower than that of the vertical-shaft kiln. Because of this drawback and certain mechanical difficulties in making the rotary joints perfectly air-tight, the CO_2 test in the gas obtained is generally lower. In the ammonia soda industry, therefore, its use is confined to the burning of the fines or caustic mud, as mentioned above. The gas then is normally not used.

The vertical-shaft kiln with mixed feed possesses many advantages. The burning zone, or decomposition zone, is well insulated and is adapted to heat regeneration both in the exit gases at the top and in the burnt stone at the bottom. The fuel economy is good and gas containing a maximum percentage of CO_2 can be maintained. The whole secret in securing capacity production for the kiln lies in the ability to use forced draft at the bottom of the kiln.

The lime as drawn from the bottom contains portions of undecomposed limestone and sometimes also particles of unburnt coke or glowing ember. The undecomposed limestone is generally in the form of hard cores in the centers of lumps of lime. The presence of such a core in a lump is often revealed by its abnormal weight. In many older plants where the kilns are relatively short for the diameter, the production of these cores is a considerable part of the total lime. Such cores are rejected by the slaker and are returned to the kiln as a regular fraction of the fresh stone charged into the kiln. Further, in short kilns, it is often extremely difficult to maintain the average gas test above 40 per cent CO_2. · The quantity of cores produced depends on the efficiency of operation of the kiln, its design and construction (as regards heat insulation, height in proportion to the diameter, etc.), and the rate at which it is operated. Even in a most efficient kiln of the modern height, a certain quantity of core will be produced above a certain operating rate.

The size of limestone for soda work varies from 2 to 6 inches; the coke is usually 2 to $2\frac{1}{2}$ inches. The ratio of fuel to stone depends largely upon the heat efficiency of the kiln, the quality of the stone, and the

calorific value of the fuel. With a tall kiln, a heavy brick lining, and good coke, the ratio of coke to stone can be as low as 1 to 16 by weight without leaving an excessive amount of unburnt core in the lime, and the gas obtained contains 41 to 43 per cent carbon dioxide. This low fuel ratio and high-test gas have been attained and maintained continuously in soda plants in kilns of sufficient height. At times, the gas test may jump to 48 or 54 per cent carbon dioxide, but this occurs only momentarily when the blast is suddenly cut off while the kiln is in full operation.

For good gas production an excess of fuel should be avoided. The carbon dioxide produced from the limestone approximates 100 per cent. Dilution is caused by nitrogen gas introduced in the air required to burn the fuel charged with the limestone. To be able to use the smallest possible quantity of fuel necessary for the proper burning of the stone, the kiln must be highly efficient in the conservation of heat and must have the necessary height. It is often a question of judgment in the operation of ammonia soda works whether one should maintain a good gas test and stand a little more returned stone.

Fuel used to burn the stone should not contain too high ash, because in the mixed-feed kiln, high ash not only contaminates the lime but also causes clinkering in the kiln. The acidic properties of SiO_2, Al_2O_3 and Fe_2O_3 in the ash tend to form fused clinkers with lime, causing clinkering between pieces of lime and adhesion of the clinker to the refractory walls of the kiln. Coke used should contain not more than 6 to 10 per cent ash, but in no case should the ash content in the coke exceed 15 per cent. Hard coke is preferred, because soft coke produces too much fines during crushing and has a tendency to be crushed in the kiln, causing excessive resistance to the blast.

The kiln should be as far as possible adiabatically isolated from its surroundings. This means heavy lining from bottom to top. There should be height enough to get a good regenerative effect. The exit gas at the top should be cooled by the incoming charge (limestone and fuel) so that its temperature is low as it emerges. The lime at the bottom should be cooled by the incoming draft and drawn out cold. In other words, both top and bottom of the kiln should be cold. The burning zone is in the region from a fourth to a third the way up from the bottom. The temperature at this point is around 1050° C., though a temperature of 1100° C. is not uncommon. The height of the burning zone depends upon how the kiln is forced, *i.e.*, how much blast is sent through, and how fast the lime is drawn. Under normal conditions the burning zone should be kept as low as is consistent with a reasonably cooled lime for drawing.

For large kilns, that is, over 14 feet in diameter with a height of more than 80 feet, the draft pressure drop is about 6 inches of water. In such kilns the distribution of air tends to be uneven. The paths of least resistance are through the coarsest particles of stone and coke. These larger pieces tend to segregate at certain places across the kiln cross-section, depending principally on the method of charging. If the stone

fed is merely dumped into a single small hole in the middle of the kiln top deck, the larger pieces roll toward the walls of the kilns where the gas resistance is in any case low because of the relatively smooth kiln walls. This type of segregation is well understood and affects many operations, such as feeding coal onto automatic stokers in wide boilers,
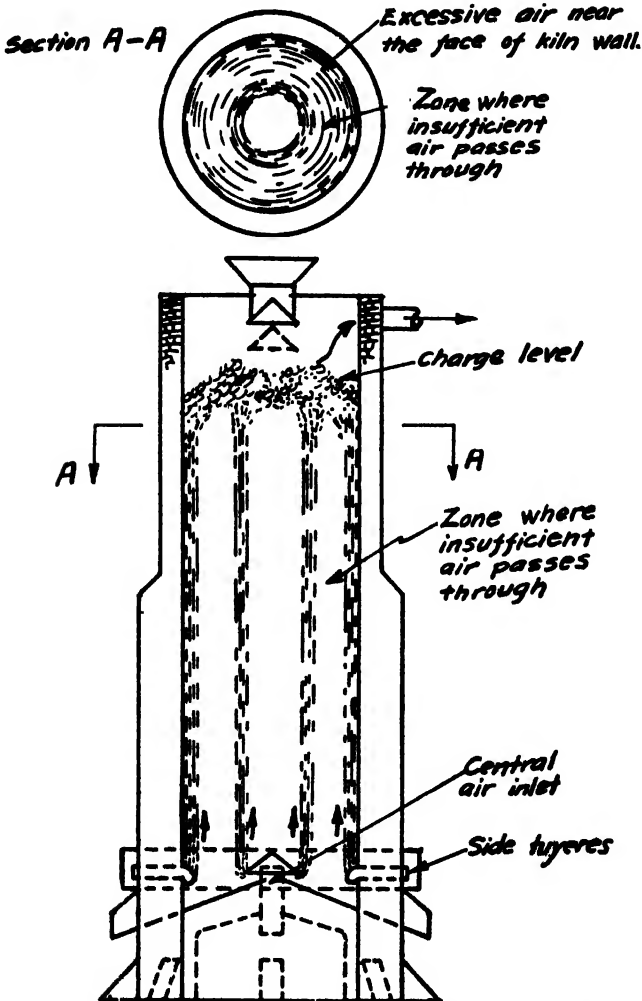
Fig. 20. Lime kiln showing normal distribution of blast.

feeding coke to a gas producer, "stock-pile classification" such as is met with in mineral operations, etc. Although the distribution of air up through the kiln can be slightly aided by proper location of tuyeres around the sides and in the center, by far the most important factor is the dis-

tribution of stone and coke uniformly over the entire kiln cross-section. The difficulty with a single hole charging device is illustrated in Fig. 20.

In mixed feed charging, when the charge is dumped onto a slope or is allowed to fall into the kiln from a 45° bell hopper, the large pieces of stone will roll forward the farthest, while the smaller ones together with
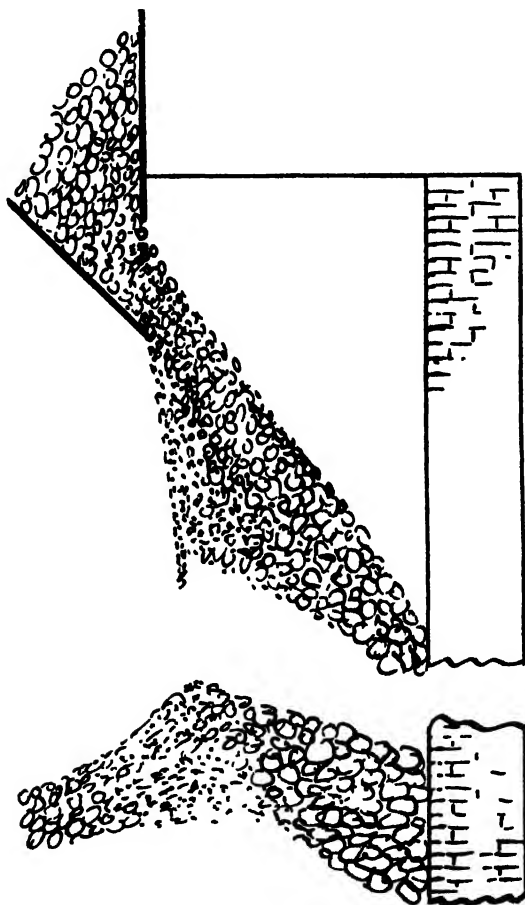
Fig. 21. Lime kiln showing tendency of different sizes of materials to segregate during charging.

the larger part of the coke will merely drop down almost vertically off the edge of the slope. Consequently, the charge is not uniform inside the kiln; the area vertically below the edge of the cone has more of the finer pieces of stone with more than its share of coke, while that farther away from the edge has most of the larger pieces of stone and yet an insufficient quantity of coke to burn them (Fig. 21).* Thus, in the zone

* This may also cause excessive wear on the surface of the kiln lining at the top by the impact of stone against the bricks.

directly under the edge of the slope, the stone becomes overburnt and considerable coke is left over, and the lime drawn is red hot. Here little air can pass through, because of the denser mass of the finer pieces of stone and coke. The result is that the fire zone stays very low in the center of the kiln. On the other hand, in the zone farther away from the edge of the cone or next to the refractory walls, air passes through more freely because of the lower resistance between the charge and the wall surface. However, because of the larger sizes of stone and of insufficient coke, the stone is only partially burned, a large core being left in each of the larger lumps. Here the fire is carried high up in the kiln, and cold but superficially burned lime is drawn at the bottom. This segregation is very serious, for under these circumstances not only is the stone not properly burned, but the gas test is also low. In such cases, experience has shown that there are not more than 30 to 32 per cent carbon dioxide in the gas obtained and 3 to 5 per cent oxygen, while 0.5 to 1 per cent carbon monoxide is also present. Typical analyses are given in Table 35.

TABLE 35. Typical Analyses of Kiln Gases under Abnormal Conditions

I		II		III	
					Slight Improve-ment Attained
	Per Cent by Vol		Per Cent by Vol		Per Cent by Vol
CO_2	30.2	CO_2	31.6	CO_2	34.6
O_2	4 6	O_2	3 6	O_2	2 4
CO	0 8	CO	0.6	CO	0.4

Such a situation is aggravated if the limestone pieces are not of nearly uniform size. This, however, puts an undue burden on quarrying operation and requires rejection of a very large part of potential quarry output. When, however, there is more than one kiln in operation, the remedy is simple. Each kiln may burn a different size of stone so that there will not be such a wide range of sizes in each individual kiln. That kiln which burns a smaller size, of course, requires a little higher wind pressure, which may be readily adjusted by means of different valves provided. But proper mechanical designing of the charging mechanism is usually the best remedy, and a very large number of ingenious devices have been introduced to accomplish this result. The simplest is the use of several charging holes in the deck of the kiln, into each of which the same amount of material is charged per unit of time. Or, an eccentric charging hopper may be used which can be revolved over a certain angle after each charge, as in a large gas producer. Other devices consist of mechanically rotating covers with the feed opening being continually moved by means of cams, etc. One of the more complicated devices consists of feed cones with spiral edges so that the angle of each element is different and is designed to produce that trajectory which gives uniform distribution. As was described on page 87, such cones are turned a certain number of degrees for each batch of feed charged over them by a skip hoist. In this way it is possible to maintain the fire zone horizontally at the same level in the kiln.

In addition to uniformity of size, it is important that the stone should be free from clay, dirt, or fine dust; otherwise the air passage may be choked, and the fine, overburnt pieces may react with clay or dirt to form clinkers. Such clinkers may attain the size of 24 inches and may completely block the lime passage at the draw opening at the bottom.

The blast used in vertical lime kilns varies widely, anything from 4 to 9 inches of water pressure having been used. It depends on the rate of operation, the size of the stone and coke employed, and the height of the kiln. With large kilns, the capacity of which is ample and the rate of burning low, less air pressure is required for operation. Taller kilns burning a wide range of sizes of stone, from which only the minus 2 in. fraction has been removed, and kilns which are being operated at high rates of production, sometimes require as much as 10 in. W.G. Smaller sizes of stone necessitate a higher blast and require less time for burning. If large amounts of the smaller sizes or fines are mixed with the larger pieces, the stone will not be evenly burned. The smaller pieces become overburnt, while the larger lumps are incompletely burned. Also, smaller pieces, or fines, tend to segregate themselves so as to choke the air passage. Consequently, when it is desired to increase the rate of operation by increasing the blast to maintain a slight positive pressure on the top of the kiln, air may blow in channels through the larger lumps of the stone so that free oxygen is found in the gas at the top of the kiln, giving low gas tests, as shown in Table 35.

From the foregoing it will be seen that to secure successful operation of a lime kiln, *i.e.*, to get a high-test gas and to secure uniformly and reasonably completely burned lime, too much attention cannot be given to the following matters:

(a) Even distribution of the fuel in the stone.

(b) Absence of segregation of smaller pieces of stone from the larger lumps.

(c) Even distribution of air in the charge.

Any tendency to segregate the fuel from the stone, or the smaller pieces of the stone from the larger ones, should be corrected at once; otherwise, as has been noted above, the gas would contain (1) an excess of oxygen, (2) considerable carbon monoxide, and (3) a low percentage of carbon dioxide. Also, there may be large amounts of unburned limestone from one side of the kiln, and at the same time overburnt lime from the other. Improvement may always be secured by having the pieces of limestone and the pieces of fuel (coke) as nearly of uniform size as possible, by adjusting the wind dampers or butterfly valves to control the amount of air admitted at different points at the bottom of the kiln, and by having the charging mechanism at the top of the kiln so designed as to let the charge in more evenly, *i.e.*, without any tendency toward segregation.

The gas from the 16- to 20-inch down-take located at the top of the kiln is drawn off by carbon dioxide compressors through a cast-iron scrubber, frequently 6 feet in diameter and about 20 feet high, with a division plate and a mushroom at the bottom above the gas inlet. Above

this mushroom section, the whole space is filled either with Raschig rings or cylindrical tiles (chemical tiles), 4 inches in inside diameter and 5 inches high, or packed with 6-inch coke, through which water trickles down from the top and gas passes up from the bottom countercurrently. Sometimes large pieces of limestone itself are used for packing, and this has a tendency to neutralize any sulfur dioxide in the gas. The scrubber not only rids the gas of all dust and tarry matter but cools it to below 30° C. on its way to the carbon dioxide compressor intake. It is important to see that there is no excessive resistance due to the depth of the wash in the passette; otherwise suction in the gas main at the compressor end would be undesirably high. For this reason, the edge of the mushroom in the scrubber should barely touch the water surface; chemical tile serves the purpose better than coke or stone packing. To adjust the amount of suction between the soda dryers and the lime kilns, if the two branches of the gas mains are connected, the level of the water in the scrubber section can be raised or lowered by means of an overflow loop or a half-moon segment at the water overflow outlet, so that the carbon dioxide compressors will draw the soda dryer gas before they draw the lean gas from the lime kilns. Also, it is frequently arranged to have a separate valve in each branch, one on the kiln gas main and one on the furnace gas main, so that the differential pressures in both branches may be set as desired and mechanically controlled in relation to each other by a sensitive automatic mechanism.

The foregoing type of kiln gas scrubber, which is ordinarily used in the ammonia soda plants, is generally incapable of removing the finest particles of dust in the gas, and as a consequence, the CO_2 gas compressor cylinders have high maintenance charges caused by frequent renewals of discharge valves, piston rod, piston, or cylinder wall liner. The best type of scrubbing with comparatively little loss of pressure through the scrubber is found to be a spiral whirlpool type of washing, such as the gas cleaner developed by the Blaw-Knox Co., which may be installed before the intake to the gas compressors so that only pure, clean gases are handled by the compressors.

The gas from the lime kiln should have the composition shown in Table 36. Excessive oxygen in the gas indicates (1) uneven air distribu-

TABLE 36.   Composition of Kiln Gas.

	Per Cent
CO_2	41-43
O_2	0.0-0.2
CO	0.0-0.0

tion or channelling in the air passage as the result of segregation of larger pieces of stone from smaller ones; (2) unequal heights of combustion zones above the different air inlets, as a result either of channelling, as stated above, or of obstruction at certain air inlets; and (3) creeping of the fire too high up toward the top of the kiln as the result of the excessive air blast employed and the low rate of lime drawing. Sometimes

the presence of oxygen in the gas is caused by a leakage of air at the top of the kiln when a partial vacuum exists there. The presence of 1 per cent or more of carbon monoxide may indicate (1) channelling in the air passage from the causes mentioned above; or (2) too high a ratio of fuel, causing a reduction of carbon dioxide by incandescent carbon just above the decomposition zone.

$$CO_2 + C \rightarrow 2CO$$
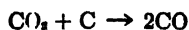
In the latter case, much of the lime, of course, would be overburnt. In the course of operation, as mentioned above, it may be found that the lime drawn from one side of the kiln comes out red hot, while at the other side it is stone cold. On the side of the kiln to which most of the air goes and in which less fuel is present to burn the stone completely, the burning zone is forced much higher, with the result that the lime is drawn out quite cold and only partially burned. The other side, in which the lime comes out red hot and overburnt, has a large excess of fuel in proportion to the limestone; and because of denser mass little air is allowed through, with the result that the fire stays low. The result of faulty air distribution may be illustrated by an incident: a 41 per cent carbon dioxide test dropped to 32 when the air which was accidentally obstructed went to one side of the kiln. This decrease occurred as soon as the obstruction took place and remained until the obstruction was removed.

All the foregoing troubles lead to a low gas test. The operation of a lime kiln in the ammonia soda industry is a delicate matter. The ability to diagnose trouble comes only through keen observation and long experience. The condition of the lime can be readily judged by its appearance and its density as felt by the hand. Well-burned lime is light in color and in weight. Partially burned lime which has a raw core is heavy. Deadburnt or overburnt lime is darker in color and denser, with the appearance of checks. For the control of the process, an hourly test of the gas is made by means of an Orsat apparatus, and the amount of returned stone (unburnt core) and that of rejected "sand" in the lime drawn are determined and recorded.

The fused mass of lime adheres to the brick walls and may build "scaffolds" against the brickwork. The descending stone then may tear off a portion of the fire brick from the face of the lining. Nothing is more detrimental to the life of the kiln than this. In the course of operation, occasionally a loud noise inside the kiln is heard due to the falling of the stone arched up over a void space. In the worst case, the "arching" and "scaffolding" may become so serious that the stone may actually be held up so that it cannot descend to make room for the charge in the top of the kiln. The abrasive action of the descending stone on the face of the fire brick is normally slight; but if the stone level inside the kiln should be allowed to fall low, the pounding of the stones falling from the top through some distance against the brickwork during charging may do considerable damage to the fire brick lining. A kiln kept only partially filled cannot give good results anyway, and means are generally provided

to gauge the level of the charge at the top of the kiln. If the kiln is kept full of the charge all the time and a fairly good quality of limestone and coke is used which have little tendency to cause serious clinkering inside the kiln, the wear and tear on the brickwork is not heavy. Such a kiln will continue to operate day in and day out without repairs for a period of three to five years.

Lumps of clinker formed in the lime by the fire brick falling from the kiln lining give the following analysis:

TABLE 37.   Analysis of Lime-Firebrick Clinker.

	Per Cent
CaO	61.00
MgO	1.96
SiO_2	17.84
Al_2O_3	16.10
Fe_2O_3	2.90

High-grade limestone is essential since impurities in the limestone cause a great deal of trouble in operation. Magnesium oxide in lime is an inert substance, although carbon dioxide gas is liberated more readily from magnesium carbonate. The presence of more than 5 per cent of silica in the limestone causes clinkering or semi-fusion, and under the worst conditions, "arching" or "scaffolding" in the lime kiln, as mentioned above, due to its reaction with lime, forming a calcium silicate:

$$xCaCO_3 + ySiO_2 \rightarrow xCaO . ySiO_2 + xCO_2$$
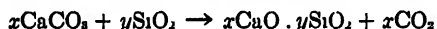
Pure lime fuses only at a temperature of about 2550° C., which is beyond the temperature range in the kiln. Alumina in the limestone has a more harmful effect than silica. Not only has it a greater tendency to lower the fusion point of lime, but it also forms a sticky paste in the lime slaker. Like silica, it enters into reaction with lime, giving a calcium aluminate (probably tricalcium aluminate) at the temperature of the burning zone.

$$3CaCO_3 + Al_2O_3 \rightarrow 3CaO . Al_2O_3 + 3CO_2$$
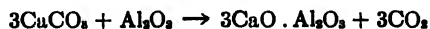
It has a tendency to reduce the temperature at which lime clinker (of cement character) is formed. Because of the quick-setting tendency of this aluminate, a rather sticky paste is formed in the slaker, clogging the passage of the milk of lime in the slaker. This may seriously interfere

TABLE 38.   Composition of Lime Clinker.
(Air-dried Sample.)

	Per Cent
CaO	75.55
$CaCO_3$	3.70
MgO	2.29
SiO_2	5.58
Al_2O_3	9.24
Fe_2O_3	0.64
Water by diff.	3.00 (due to exposure)

with the slaking operation and consequently the distiller operation, with the result that normal strength of the milk of lime cannot be maintained and the lime pipes and pumps are clogged.

Table 38 shows the composition of the dark-colored, semi-fused clinker in the lime drawn from the kiln.

The composition of the limestone yielding such clinker can be calculated, with the results given in Table 39.

TABLE 39. Composition of Limestone Forming Clinker.

		Per Cent
$CaCO_3$		87.30
$MgCO_3$		3.02
Silica	3.52 ⎫	
Ferric oxide	0.40 ⎬ 9.73	
Alumina	5.81 ⎭	

The sticky lime paste formed in the slaker which stops the passage of the milk of lime at the discharge has the composition shown in Table 40.

TABLE 40. Composition of Sticky Lime P

	Per Cent
CaO	27.80
$CaCO_3$	9.64
MgO	2.35
SiO_2	4.47
Fe_2O_3	0.24
Al_2O_3	2.73
Water by diff.	52.73

Calculated to limestone, the composition of the limestone is given in Table 41.

TABLE 41. Composition of Limestone Calculated from the Sticky Lime Paste.

		Per Cent
$CaCO_3$		82.80
$MgCO_3$		6.87
Silica	6.24 ⎫	
Ferric oxide	0.34 ⎬ 10.39	
Alumina	3.81 ⎭	

It is obvious from the foregoing that any stone containing as much as 10 per cent silica, alumina and iron is substantially impossible to burn successfully in an ammonia soda plant. Occasionally, high-silica (quartzite) and high-alumina (clay) limestone escapes attention through the quarrying and washing operations and reaches the kiln, with momentary results in the plant operation as described above.

The down-take for gas at the kiln top and the gas inlet to the scrubber are frequently clogged with lime dust which comes over with the gas. At these points, instead of "elbows," "tees" are used with blind flanges which can be removed for cleaning when necessary. When the "tee" at the top

of the kiln is choked by dust, the vacuum becomes excessive in the down-take pipe below. When, however, the gas inlet at the bottom of the scrubber is choked, the vacuum at the top of the scrubber or inside the scrubber will be high. The point of constriction can be located by spotting the vacuum readings at different points (at which water manometers should be provided). At times, it will be found that the vacuum at the carbon dioxide compressor suction main is high, but the kiln top is still under considerable pressure. This is the time to look for choking at different points in the kiln gas down-take, at the inlet to the scrubber, and at the bottom of the scrubber, caused by the accumulation of dust from the gas. In this case, the vacuum in the scrubber above the bottom section would be high, but the gas down-take leading to the inlet at the bottom of the scrubber would be under pressure. On the other hand, when water used in the scrubber is low, or when for some reason the water spray at the top of the scrubber is cut off, the seal at the bottom of the scrubber may be lost and air may rush in through the water overflow opening at the scrubber bottom in large volumes, so that considerable pressure would be felt at the soda furnace end. All these things interfere with satisfactory operation, and demand close attention and prompt correction.

Well controlled soda plants have posted the pressure drop for the gas through every part of the system when the part is reasonably clean. Shut-downs for cleaning operations are planned when certain predetermined increases are reached. The cleaning of the gas from lime kilns is an expensive and never completed operation. The residual dusts find their way through the system and, besides introducing high pressure drops in the various parts of the system, may cause high maintenance costs in compressor operation.

In soda works the lime for distillation is slaked to a thick milk, containing 200 to 250 grams per liter CaO. The slaking can be done in a large steel tank provided with a stirrer. Lime is charged into a steel basket immersed in the water in the tank. The stirring action aids the disintegration of the lumps and carries the fine particles in suspension. Unburnt core is caught in the basket. The machine now most commonly used, however, is the rotary slaker which has a large capacity and is continuous in operation. It is of the general rotary type, having two support points. The shell may be made of $\frac{1}{4}$-inch steel plates, 5 by 6 feet inside diameter and 40 to 50 feet long, having a lining. The revolving shell is provided with a number of short sections of angle iron flights to carry the solids forward to the discharge end. It works on the counter-current principle, lime entering the discharge end and water the tail end, where it serves also to wash the "sand" and unburnt core as these are carried out by a ribbon conveyor. Such a rotary slaker has a capacity of 200 to 250 tons of limestone per 24 hours. The unburnt stone is charged back to the kiln and the "sand" which is rejected makes a good road-filling material after it is allowed to age by exposure. If the limestone is of low grade, containing sandstone, clay, etc., the returned stone will

consist mostly of these impurities having little limestone distributed in the mass. Under these conditions it is wise to reject these stones instead of charging them back to the kiln with the fresh stone. Besides sand and other silicious matter, the "sand" consists of large amounts of fine lime that have been overburnt and have passed through the slaker without being slaked. Generally it will be found that this overburnt lime slowly disintegrates on exposure to the air (two or three days), when it will pay to send it through the slaker again.

Many slakers, however, do not operate on a perfect counter-current principle. Both lime and water (*i.e.*, well over 90 per cent of the water) enter at the discharge end and travel through an inner shell for about ¼ or ⅓ of the length of the slaker. The milk of lime is drawn from between the inner and outer shells at the same end. The slowly digesting and the undigested matter is propelled to the back, so that it has a very long time to give up all its suspended particles to the milk. At the back end it is lifted up into a conical section and finally into a cylindrical screen section, where the remaining small amount of water (*i.e.*, about 10 per cent of the total) washes it free of the adhering CaO. In most of these plants the quantity of cores and rejects from the slaker is very small, and these are not returned to the kiln. They are occasionally ground up and added to the milk of lime, when and if they consist mostly of overburnt particles. Grinding decidedly makes the overburnt lime more available.

Steam is saved at the ammonia distilling operation if the milk of lime is used hot. In well regulated plants, lime reaches the prelimer at a temperature above 80° C. At lower temperatures not only is an excess of steam used, but the prelimer reaction is slower, and there is a greater tendency toward the formation of scales. The slaking operation is exothermic enough so that milk of lime is automatically produced at almost 100° C. However, unless the slaker is well designed and all pipe lines and storage tanks for milk of lime are thoroughly insulated, this temperature falls rapidly because of air cooling. The water used for slaking should be at a high temperature, to facilitate the operation and increase the capacity of the slaking apparatus. Cold water and cold lime often refuse to react when a slaker is just being started anew. There are several sources of hot water for the slaking operation, the commonest being the condenser water from the distillation operation. Theoretically, the water for the slaking operation would be heated to over 100° C. from the heat of hydration, and the steam formed is removed via the slaker stack. The hot milk of lime can be handled by means of plunger pumps or centrifugal pumps. The duty of the pumps is quite severe because of the suspended abrasive particles, or "sand," in the milk of lime. Large, well-designed centrifugal pumps with open impellers and renewable sleeves, designed for low-cost replacement, work successfully. To prevent the pumps from clogging, the milk of lime is screened immediately after slaking. The over-sized particles retained on the screen are washed with a small amount of water and then added to the rejects from the slaker before grinding for recovery, or before sending to waste.

Milk of lime storage reservoirs generally consist of steel or concrete tanks, well insulated and provided with mechanical agitators.

In the practical construction of the lime kiln, the top cover with the charging hopper and cone is never air-tight. Consequently it is necessary to carry a positive pressure of about ⅛ inch of water at the top, so that leakage will be from the kiln to the air rather than from the air to the kiln with resulting dilution of the gas. Also, an atmospheric vent pipe is provided so that, in case of any excess of lean gas, the kiln gas can be let out to the atmosphere in order that the dryers may have sufficient suction to pull out the gas from them. In the case of rotating kiln tops in large kilns, however, the charging mechanism is sealed with water or mineral oil against leakage at a low vacuum. During the periodic charging operation, the gas may be temporarily turned to the atmosphere and kept entirely off the gas main.

Table 42 gives the approximate capacities of mixed-feed, vertical-shaft lime kilns. It is understood that the capacity of a kiln for a given set of dimensions depends upon many factors. It depends upon the quality of the stone charged, the use of a forced draft, the use of a mechanical discharge mechanism, the grading of the sizes of the stone and coke in the charge, etc.

TABLE 42. Capacity of Mixed Feed, Vertical-shaft Lime Kilns.
(Working on good grade of limestone with forced draft and mechanical discharge.)

Inside Dimensions of Kiln		Thickness of Lining			Tons of Limestone
Diameter	Height	ttom	Top	Average	Burning per 24 Hours
Feet		Inches			
10	60-70	30	18	24	120-150
12	80-90	42	30	36	200-250
14	90-100	48	36	42	300-350
16	120	54	42	48	400-500

Large kilns are more economical in the utilization of heat, because heat losses by radiation and convection are proportional to the surface exposed (the square of the linear dimensions), whereas the capacity is more nearly proportional to the volume (the cube of the dimension), since the height of the kiln is more or less dependent on the diameter. On the other hand, in the case of very large kilns, there is greater tendency for the segregation of the stone and coke and for uneven distribution of the air current throughout the whole cross-section of the kiln. To get the fullest advantages of very large kilns, therefore, requires the introduction of a refined mechanism for an adequate feed distribution, automatic lime discharge, and blast distribution and regulation.

BURNING OF ANOTHER FORM OF LIMESTONE

Other forms of limestone have been known. In fact, lime in China was produced for centuries by burning oyster shells; and this source of lime was known much earlier than the lime rock there. However, the application to the ammonia soda industry of oyster shells as a source of

lime is a recent one. On the Gulf Coast of North America, a special form of oyster shells found in abundance has been used in the ammonia soda industry since the new soda industry was established there. At first, attempts were made to use the same shaft kiln, but these met with failure. Rotary kilns are now used for the burning of such oyster shells there. However, the operation is attended by the same characteristics as in the burning of the fines from a limestone quarry in any rotary type kiln. If the larger shells are screened out from the smaller ones, the larger shells may be burned satisfactorily in the vertical shaft kiln, provided some limestone is mixed with them for burning. Therefore it is often seen that when these oyster shells are used, both the rotary kiln and the vertical shaft kiln are employed side by side.

Oyster shells are an important source of limestone along the American Gulf Coast, where sedimentary deposits of limestone are deeply buried under later deposits and alluvial strata. Oyster shells in the South have been used since Colonial times as a source of agricultural lime along much of the American seacoast. The oyster breeds along shores where the water is not entirely salty. Occasionally nature, through flood or excessive rainfall, makes the water too fresh for the oyster to survive. Reefs of shells are found along substantially all seacoasts, particularly near the mouths of streams or bays, into which fresh-water streams empty. Through metamorphic pressure of superimposed strata, such reefs of oyster shells have become compressed and eventually turned into limestone. It is, therefore, to be expected that the chemical analysis of the oyster shells will be similar to that of limestone. A sample of thoroughly washed oyster shells is hardly distinguishable from a high-grade low-magnesium limestone by a chemical analysis of the principal inorganic constituents. The following table gives an analysis of a sample representative of each on the dry basis:

TABLE 43. Comparison of Chemical Analyses of Oyster Shells and Limestone.

	Oyster Shells (Gulf Coast)	Limestone (Amherstburg, Canada)
Calcium carbonate, $CaCO_3$	96.05%	96.70%
Magnesium carbonate, $MgCO_3$	1.22	2.11
Calcium sulfate, $CaSO_4$	0.36	0.05
Alumina oxide and iron oxide, R_2O_3	0.33	0.57
Silica, SiO_2	1.28	0.52

The above limestone is, of course, "high-grade," that is, it is from a deposit which contains very little earthy matter and has been thoroughly washed. Relatively few deposits are so low in magnesium. Oyster shells as dredged generally contain appreciable quantities of organic matter.

Oyster shells present problems in the burning of lime and CO_2 gas for the ammonia soda operation, which are unique to this form of calcium carbonate. The shaft kiln, which is the standard equipment in the ammonia soda plant for burning limestone, is not suited to burning shells. The individual pieces of oyster shells are so small that there is an exces-

sive pressure drop in the air-blast. The organic material, and probably also silica in the shells, combine to cause the formation of large aggregates of clinkers. Furthermore, since the shells are thin and fragile, they are easily crushed, and so they are not suitable to the operation of shaft kilns of modern height. From the standpoint of the ammonia soda industry, it would be desirable to develop a shaft kiln suitable to oyster-shell burning. Agricultural oyster-shell lime has been produced in short shaft kilns, but since the development of the rotary type of cement kiln, shells have been burned on a large-scale commercial basis in that type of equipment.

Oyster shells require no special preparation before burning in a rotary kiln. Depending only on the purity of the lime desired, they are washed in conventional types of washing equipment. The process of collecting the shells when dredged by a dredger is in itself a washing operation. When very high-grade white finishing lime is desired, the shells are given a thorough supplementary washing and generally also a crushing operation, to dislodge dirt particles deposited in the crevices of the shells. In the ammonia soda industry, the process can stand a certain amount of impurity in the lime from the shells as dredged. The shells are therefore not crushed and, except for the washing received on the dredge, are not washed. The shells, as fed to the kiln, contain up to 8 per cent moisture, depending upon the length of time they have been in storage at the plant.

The kiln is a long rotating cylinder, set on a slope of $\frac{1}{2}$ inch per foot. The main equipment is similar to that used in the burning of caustic mud in caustic soda manufacture (see Chapter XIX), but more particularly in the burning of raw mix in dry-process cement manufacture. The kiln must be considerably longer than the usual apparatus of this type, because a higher fuel efficiency is justified in order to obtain gases rich in CO_2. For the same reason, it is important to cool the discharged lime for preheating the air required for combustion. This entails a separate lime cooling apparatus, similar to the rotary clinker coolers used in the cement manufacture. However, as the gas is also wanted, the kiln must be closed at both ends.

The shells are fed into the high end of the kiln by means of a constant-weight feeder and the gases emerging from this end of the kiln are handled just like vertical kiln gases, except that a dust separation in the hot and dry state precedes the usual scrubbing. The shells, in their slow progress down the kiln, are first freed from surface moisture, then gradually are preheated to the calcining temperature, and finally in direct contact with a pulverized coal, oil or gas flame, are calcined and discharged to the cooler. Air is blown and drawn through the shell lime in the cooler. A part of the air preheated in the cooler is drawn off and used as "primary air" for injecting the fuel through the burner into the kiln. The rest of the air goes directly from the cooler to the kiln hood, which is kept under accurately balanced pressure by a delicate control mechanism. The primary control of this operation is affected by the

speed of rotation of the kiln. The oyster-shell feeder is electrically or mechanically interlocked with the kiln drive, and the speed at which fuel is injected is likewise accurately proportioned to the kiln speed. Increase or decrease in fuel is based on a combination of factors which include:

(a) analysis of the lime discharged,
(b) temperature of the lime to the cooler,
(c) analysis of the gases obtained.

If the discharged lime drops in CaO content (or increases in CO_2 content), it is generally an indication of insufficient fuel. It may be an indication of faulty fuel-air ratio, which can be determined from an analysis of the gases. If CO has increased, there is insufficient air; whereas if too much O_2 is present, this is indicative of excess air. Any out-of-control condition results in a lowered CO_2 concentration in the gases. Hence this decrease in concentration is generally the first indication of maladjustment of some operating factor.

The cooled shell lime discharged from the coolers is conveyed and elevated to the bins located above the slaking apparatus. The slaking of oyster-shell lime is essentially the same as that of stone lime. The physical properties of the milk of lime are similar to those of any low-magnesium limestone milk.

Partly because of the large amount of kiln surface from which heat is radiated relative to lime burning rate, the unit fuel consumption of the rotary kiln is appreciably higher than that of the shaft kiln. Consequently, the strength of the CO_2 gas is lower, which requires more compressing power for the carbonating towers. These effects can be held to a minimum only through the very best design of equipment which will permit extremely accurate control and very quick response to control. Whereas in the very large and tall shaft kilns used in the ammonia soda industry, good operating conditions are almost impossible to upset by a short-time maladjustment, the rotary kiln is extremely sensitive to changes in blast pressure, suction pressure, rate of shell feed, fuel-to-shell ratio, fuel-to-air ratio, etc. The following table gives some estimated operating data for kilns burning oyster shells with various kinds of fuel:

TABLE 44. CO_2 Gases from Oyster Shells Using Different Forms of Fuel.

Form of Fuel	Alabama Coal	Petroleum Coke	Bunker C Oil	Natural Gas 1150 B.t.u.
Net B.t.u. consumption per ton dry oyster shells	3,000,000	2,990,000	3,020,000	3,400,000
Kiln Gas Analysis				
CO_2	34.4	36.0	32.9	28.1
O_2	0.4	0.4	0.4	0.4
CO	0.2	0.2	0.2	0.2
Lb. CO_2 per short ton of dry oyster shells	1470	1497	1390	1290

Because of the high calcium content of the shells, the consumption per ton of ammonia soda is lower than that for plants using ordinary limestone. A total consumption of 1.15 tons of shell per ton of soda ash

represents good actual practice, and compares with 1.45 in a plant whose stone contains 8 to 10 per cent magnesium carbonate, and with 1.25 in a plant which uses a high-grade, low-magnesium stone.

Since oyster shells are a peculiarly thin form of limestone, heat is able to penetrate all the way through with considerable rapidity; therefore the kiln required to burn the oyster shells adequately (that is with very little CO_2 left in the lime) need not be very long. The length of the kiln should be sufficient to exchange properly the sensible heat of both the gases of combustion and decomposition with the oyster shell feed on its way to the calcining zone. Only by good heat regeneration can the fuel consumption be kept down to anywhere near vertical kiln practice. Excess fuel requires oxygen to burn it, and this oxygen brings nitrogen from the air into the kiln, thus diluting the gases. For the same reason, as much as possible of the kiln cylinder itself should have a good layer of insulating material (such as Sil-O-Cel) between the refractory lining and the steel shell.

The lime kilns in ammonia soda plants must always operate to suit the demand of both lime and CO_2 gas in the distillation and carbonation processes. With vertical kilns, in which there is a very large volume of preheated stone and burned lime, changes in the demand of either gas or lime that are of ordinary duration generally only raise or lower the burning zone. Normally there is an excess of CO_2 gas in an alkali plant. In some of the kilns during a part of the time of operation, the gas is turned to the atmosphere, thus avoiding any dilution, which might take place during periods of increased gas demand.

With the rotary kilns this type of control is impossible. There is only a small amount of material in the kiln. A gas holder is therefore placed between the kiln and the CO_2 compressor suction. The kiln is then operated as required by the reservoir levels in the dry lime and milk of lime systems. This requires extremely precise control of kiln cylinder speeds. In this respect oyster shell burning is very different from other kiln operation. Its rate of operation is controlled for instantaneous needs rather than for predetermined optimum rates.

TABLE 45.   Quality of Lime Obtained from Oyster Shells and Limestone.

	Oyster Shell Lime (Gulf Coast)	Limestone Lime (Amherstburg, Canada)
CaO (total)	89.3	75.0
$CaCO_3$	5.6	21.2
$CaSO_4$	0.7	0.3
SiO_2	2.2	0.4
R_2O_3 (combined oxides)	0.6	0.7
MgO	1.1	1.6

The kiln speed therefore establishes the primary impulse for all other operating controls. Gas pressures throughout the system are under interlocking control and excess CO_2 vents out automatically. Momentary deficiencies of CO_2 are handled by the gas holder. Table 45 above shows

a comparison of limes obtained from the oyster shells and from a good grade limestone.

From the above, it may be noted that the CO_2 gas obtained from the burning of the oyster shells in a rotary kiln is, on the whole, much weaker than that obtainable from the burning of limestone in a vertical shaft kiln of modern height. This is a handicap for an ammonia soda plant depending on oyster shells for its source of lime and CO_2 supply, although shell lime obtained is of the first quality; because weak gas for the ammonia soda manufacture has several disadvantages, as will be pointed out later on.

Kiln Calculations: Vertical Shaft, Mixed Feed Kilns

As remarked above, the kiln lining must be thick and the kiln must have a good regenerative effect both at the top and the bottom. Following are causes for the loss of heat:

(a) unburned fuel in the lime drawn out,
(b) radiation and convection losses from the body of the kiln outside,
(c) heat left in the lime drawn out,
(d) heat left in the gases emerging from the top of the kiln.

Good kiln operation requires cold conditions both at the top and the bottom. Items (c) and (d) can be determined from the specific heats and the temperature ranges. Item (a) can be only roughly estimated but generally the unburned fuel is so small that it can be assumed that all the fuel charged is burned. Item (b) can only be established by an assumption.

The following is a typical calculation of the theoretical percentage of coke required and the percentage of carbon dioxide in the gas obtained. Given (limestone and coke on moisture free basis):

Limestone	Per Cent	Coke		Per Cent
CaCO₃	89.90	Fixed carbon	*	85.25
MgCO₃	5.94	Ash		14.75
Silica and silicious matter	4.16			

Temperature of reaction zone	1050° C.
Temperature of exit gases ($N_2 + CO_2$)	80° C.
Temperature of lime drawn	50° C.
Temperature of air and limestone each	15° C.
Average specific heat of exit gases	0.23
Average specific heat of lime	0.19 *
Average specific heat of limestone	0.22 *
Average specific heat of coke	0.20
Average specific heat of air	0.2389 (or 0.24)

* N. V. S. Knibbs, "Lime and Magnesia," London. Ernest Benn, Ltd. (1924), pp. 37-38.

Under normal conditions no appreciable amount of carbon monoxide is found in the kiln exit gases, so we can assume that all carbon burns to carbon dioxide, and we shall assume also that all the carbonates in the limestone are completely decomposed.

(a) Unburned fuel in the lime: The unburned fuel present in the lime is an indefinite quantity but generally it should be very small. If the kiln is not being drawn too fast, with a proper fuel ratio, the lime should come out comparatively cold, and no unburned fuel, such as pieces of unburned or glowing coke, should come out with the lime.

(b) Radiation and convection losses from the kiln surface: With a heavy lining, the outside of the kiln is quite cold except for a section at the reaction zone, and the loss of heat is also small. Estimates have been made which would put the losses at 10 per cent of the heat input of the kiln. While the temperature inside and outside can be measured, the most uncertain factor is the thermal conductivity of the combined path through the fire-brick and common-brick wall, the sand space (or insulating material) and the casing, on account of their unknown physical character, such as looseness of material, air space, etc. It is probably safe to estimate that 10 per cent of the total heat generated should be considered as lost.

(c) Heat left in the lime drawn out: The red-hot lime should be cooled by the incoming air before it is drawn out. It will be shown that there is more than enough air to cool the lime. Let us consider that the lime comes from the burning zone at 1050° C. and that it is to be cooled down to 50° C. before it is drawn. Let us further consider that we use 150 lbs. of coke (85.25 per cent fixed carbon) per 2000 lbs. of stone (89.90 per cent $CaCO_3$ + 5.94 per cent $MgCO_3$). 100 kg. of limestone will yield

$$(100 - 89.9 - 5.94) + 89.9 \times \frac{56}{100} + 5.94 \times \frac{40.3}{84.3} + 7.5 \times .1475 = 58.4 \text{ Kg.}$$

of "lime" including the ash from the coke. The specific heat is 0.19. Therefore heat to be drawn from the lime per 100 kg. of limestone is

$$58.4 \times (1050 - 50) \times 0.19 = 11,100 \text{ kg. Cal.}$$

This 100 kg. of limestone takes 7.5 kg. of coke or 7.5 × 0.8525 fixed carbon which requires for combustion

$$\frac{7.5 \times .8525}{12} \times 32 \times \frac{1}{0.231} = 73.7 \text{ kg. of air.}$$

The specific heat of air is 0.2389. If air is preheated from 15° C. to 800° C. it requires 73.7 × 0.2389 × (800 − 15)° C = 13,750 kg. Cal. So there is generally not enough heat in the lime to preheat all the air if the heat interchange is good.

(d) Heat in the exit gases: On the other hand, there is not enough limestone to cool the exit gases. Using the same assumption as above, we have

$$73.7 + 7.5 \times 0.8525 + 89.9 \times \frac{44}{100} + 5.94 \times \frac{44}{84.3} = 122.7 \text{ kg.}$$

of gases per 100 kg. of stone. The specific heat of this mixed gas (CO_2 + N_2) can be taken as 0.23. Therefore to cool the gases from 1050° to 15° C. it would require to take away heat = 1035 × 0.23 × 122.7

= 29,300 kg. Cal. But there are 100 kg. of limestone with 7.5 kg. of coke to be taken in. Since the specific heat of coke = 0.20 and the specific heat of limestone = 0.22, if it could be heated from 15° to 1050° C., it could only extract heat = $1035 \times 0.22 \times 100 + 1035 \times 0.2 \times 7.5 = 24,350$ kg. Cal. So, granting good heat interchange and the maximum possible heat extraction, not all of the available heat in the kiln exit gases can be utilized by the incoming charge (stone and coke)—an unavoidable large item of heat loss in the kiln operation.
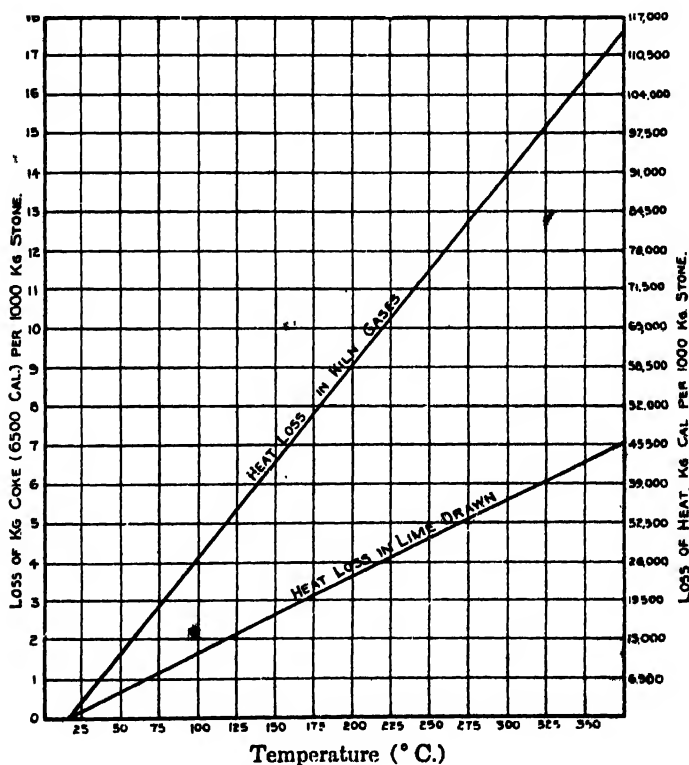
FIG. 22.   Heat loss in kiln gases and lime drawn.

From the above it can be seen that the exit gases at the top must necessarily be at a much higher temperature than the lime drawn at the bottom, if there is no loss of heat due to radiation and convection at the top portion of the kiln. This is the reason for having a tall kiln with a storage space for preheating the charge and explains the modern tendency to increase the height of the kiln. It is also the basis for the theory (confirmed by actual practice in the kiln operation) that the reaction zone must be kept as low in the kiln bottom as is consistent with a fairly cold lime draw. There is so much surplus heat (as sensible heat) in the exit gases that probably not more than 75 per cent of it is recovered even in a

tall kiln (height $\geqq$ six diameters) with the reaction zone kept about a fourth of the height from the bottom of the kiln.

Fig. 22 shows heat losses in the kiln gases and lime drawn respectively at any given temperature. These losses are practical values which will allow certain range of variation in the conditions of operation.

Based on the analyses of stone and coke as given before, the ratio of fuel to stone may be determined as follows:

Let X = kg. of coke required for every 100 kg. of stone. Let the temperature of lime drawn be 50° C. and that of the kiln exit gases 80° C. The rest of the data is given in the foregoing example. Let it further be assumed that 10 per cent of the heat be lost by radiation and convection in the kiln body and top. Starting and ending at 15° C., we have

(1) Heat required to decompose $CaCO_3 = \dfrac{89.9}{100} \times 42,900 = 38,600$ kg. Cal.

(2) Heat required to decompose $MgCO_3 = \dfrac{5.94}{84.3} \times 28,900 = 2035$ kg. Cal.

(3) Heat lost in the lime drawn at 50° C. = $[57.3 + (1.00 - 0.8525)X] \times 0.19 \times (50° - 15°) = (57.3 + 0.1475X) \times 0.19 \times 35°$ C. (57.3 is the crude lime from 100 kg. limestone.)

(4) Heat lost in the exit gases = sp. ht. $\times$ (wt. of air + wt. of carbon + wt. of CO_2 from $CaCO_3$ & $MgCO_3$) $\times$ diff. temp. =

$$0.23 \left[\frac{0.8525X}{12} \times \frac{32}{.231} + 0.8525X + 42.6 \right] \times (80 - 15) = 14.95\,(10.70X + 42.6)$$

(5) Heat losses by radiation and convection assumed at 10 per cent of the heat put in.
$\therefore$ Total heat required =

$$\frac{38,600 + 2035 + (57.3 + 0.1475X) \times 0.19 \times 35 + 14.95\,(10.70X + 42.6)}{0.9}$$

$$= \frac{40,635 + 161X + 1018}{0.9}\ \text{kg. Cal.} = \frac{41,653 + 161X}{0.9}\ \text{kg. Cal.}$$

Against this, we have the heat of combustion of X kg. of coke (85.25 per cent carbon) = $\dfrac{97,000 \times 0.8525X}{12}$ kg. Cal.

$$\therefore \frac{97,000 \times 0.8525X}{12} = \frac{41,653 + 161X}{0.9} \tag{1}$$

or $6039X = 41,653$

$\therefore X = 6.91$ kg. of coke per 100 kg. of stone or 138.2 lbs. of coke per 2000 lbs. of stone for the charge.

Therefore the heat efficiency of the kiln

$$= \frac{\text{heat used to decompose } CaCO_3 \text{ and } MgCO_3}{\text{Total heat put in}} \times 100$$

$$= \frac{40,635}{6.91 \times 0.8525 \times \dfrac{97,000}{12}} \times 100 = 85.5\%$$

The weight of "lime" obtained = $57.3 + 0.1475 \times 6.91 = 58.3$ kg. per 100 kg. stone or 58.3%.

$\therefore$ % CO_2 in the kiln gas (by volume)

$$= \frac{\dfrac{89.9}{100} + \dfrac{5.94}{84.32} + \dfrac{6.91 \times 0.8525}{12}}{\dfrac{89.9}{100} + \dfrac{5.94}{84.32} + \dfrac{6.91 \times 0.8525}{12} \times \dfrac{1}{0.209}} \times 100$$

$$= 100 \times \frac{0.899 + 0.0704 + 0.491}{0.899 + 0.0704 + 2.350} = 44.0\% \tag{2}$$

This is the theoretical percentage of carbon dioxide, assuming no excess of air and no carbon burnt to carbon monoxide and that the kiln exit gas temperature is 80° C. and the lime draw temperature 50° C. The above figures afford valuable guide in ascertaining what the kiln should do. The limiting case is when there is no loss of heat by radiation or convection from the kiln, *i.e.*, when the brick lining of the kiln is so thick that the outside casing is cold and the heat losses are negligible. Under such conditions with the same grade of stone and coke and with the same set of operating conditions in the kiln as above, Equation (1) becomes

$$\frac{97{,}000 \times 0.8525X}{12} = 41{,}653 + 161X$$

$$6729X = 41{,}653,$$

$$X = 6.19 \text{ kg. coke per 100 kg. of limestone}$$

This gives **124 lbs.** of coke per 2000 lbs. of limestone as the limiting burden under such conditions. Equation (2) then becomes

$$\% \text{ CO}_2 \text{ in the gas} = \frac{0.899 + 0.0704 + \dfrac{6.19 \times 0.8525}{12}}{0.899 + 0.0704 + \dfrac{6.19 \times 0.8525}{12 \times 0.209}} \times 100$$

$$= 45.8 \text{ as the limiting case.}$$

Again consider a general case and let

$$C = \% \text{ CaCO}_3 \text{ in limestone by wt.}$$
$$M = \% \text{ MgCO}_3 \text{ in limestone by wt.}$$
$$X = \% \text{ coke on the weight of limestone charged}$$
$$y = \text{fixed carbon in coke (expressed as fraction)}$$

On the basis of 100 kg. of limestone charged:

(1) Heat required to decompose CaCO$_3$ $= \dfrac{C}{100} \times 42{,}900 = 429C$ kg. cal.

(2) Heat required to decompose MgCO$_3$ $= \dfrac{M}{84.3} \times 28{,}900 = 343M$ kg. cal.

(3) Heat lost in lime drawn at 50° C. $= [0.56C + 0.479M + 100 - C - M + (1 - y)X] \times 0.19 \times (50 - 15)$
$= [100 - 0.44C - 0.521M + (1 - y)X] \times 6.65$

(4) Heat lost in exit gases $= 0.23\left[\dfrac{yX}{12} \times \dfrac{32}{0.231} + yX + 0.44C + 0.521M\right] \times [80 - 15]$
$= 14.95 \ (11.53yX + yX + 0.44C + 0.521M)$
$= 14.95 \ (12.53yX + 0.44C + 0.521M)$

(5) Heat lost by radiation and convection from kiln assumed at 10% of total put in.

Total heat required

$$= \frac{429C + 343M + [100 - 0.44C - 0.521M + (1 - y)X] \times 6.65}{0.9}$$

$$+ \frac{14.95 \times (12.53yX + 0.44C + 0.521M)}{0.9}$$

$$= \frac{432.7C + 347.3M + 6.65X + 181yX + 665}{0.9} = \frac{97{,}000yX}{12}$$

$$\text{or} \quad 432.7C + 347.3M + 6.65X + 665 = 7094yX$$

With the ordinary grade of coke used in the ammonia soda industry, the term $6.65X$ is small compared with $7094yX$ (being only about 0.10-0.12%). So we can write the equation (with an error within 0.12%)

$$7094yX = 432.7C + 347.3M + 665$$
$$\text{or} \quad 100yX = 6.10C + 4.90M + 9.38 \tag{3}$$

Therefore for a given grade of limestone and a given set of kiln operating conditions, X *varies inversely as* y. In other words, *given a grade of limestone, the amount of coke used varies inversely as its fixed carbon content.* The percentage of CO_2 in the gas then (assuming 10% heat loss)

$$= \frac{\dfrac{C}{100} + \dfrac{M}{84.3} + \dfrac{yX}{12}}{\dfrac{C}{100} + \dfrac{M}{84.3} + \dfrac{yX}{12 \times 0.209}} \times 100$$

$$= \frac{\dfrac{C}{100} + \dfrac{M}{84.3} + \dfrac{0.0610C + 0.0490M + 0.0938}{12}}{\dfrac{C}{100} + \dfrac{M}{84.3} + \dfrac{0.0610C + 0.0490M + 0.0938}{12 \times 0.209}} \times 100 \text{ from (3)}$$

$$= \frac{1.508C + 1.593M + 0.782}{3.43C + 3.13M + 3.74} \times 100 \tag{4}$$

Therefore *the percentage of carbon dioxide in the gas obtained,* assuming all the carbonates in the stone are decomposed and no carbon monoxide is present in the gas, *is a function only of the percentages of $CaCO_3$ and $MgCO_3$ in the stone.*

From Equation (3) we know *% fixed carbon in coke × % coke on the stone = $6.10C + 4.90M + 9.38$.* This expression is useful in calculating the amount of coke that should be required for the kiln operation, knowing the analysis of the coke and the composition of the stone.

Expression (4) enables us to determine the percentage of carbon dioxide in the gas that should be obtained from the lime kilns, knowing the composition of the limestone being burned, *i.e.,* % $CaCO_3$ and % $MgCO_3$.

When the kiln lining is so extraordinarily thick that the outer casing is cold throughout, even at the reaction zone, the heat losses by radiation and convection are negligible. Then Equation (3) becomes

$$100yX = 5.48C + 4.40M + 8.42 \tag{5}$$

and Equation (4) becomes

% CO_2 in the gas obtained $= \dfrac{1.457C + 1.551M + 0.701}{3.185C + 2.938M + 3.357} \times 100 \tag{6}$

From Equation (6) the theoretical maximum possible percentage of CO_2 in the kiln gases assuming no losses by radiation and convection from the kiln (with 80° C. exit gas temperature and 50° C. lime temperature) can be calculated whenever the composition of limestone ($CaCO_3$ and $MgCO_3$) being burned is known. Also, it should be noticed that, other conditions being equal, a high magnesium stone gives a better gas. From

Equation (6), a 100 per cent $CaCO_3$ stone gives a theoretical maximum gas test of 45.6 per cent CO_2 by volume; whereas a 100 per cent $MgCO_3$ stone gives a theoretical maximum gas test of 52.4 per cent. Stones having various percentages of $CaCO_3$ and $MgCO_3$ have theoretical maximum gas tests ranging between these two limits.

Close perusal of the above mathematical relationships should make it apparent that the last 2 or 3 per cent in the percentage of carbon dioxide above 40 per cent calls for a tremendous effort in the lime kiln operation. Further, since lime kilns generally furnish a larger portion of carbon dioxide for the column operation than the dryers, a drop of 2 to 3 per cent of carbon dioxide in the kiln gas materially lowers the percentage of carbon dioxide in the mixed gas obtained. Consequently, if only a weak gas is obtainable from the lime kilns, the consumption of salt (from the poor decomposition in the columns), of ammonia (from the ammonia losses in the cycle per ton of soda made), of the limestone used and of coke to burn the limestone, of the power required in the CO_2 compressors to force the gas through the columns—in fact of most of the important items in the manufacture of soda ash—will be high and the efficiency of the whole operation will drop off. Hence lime kiln operation occupies no minor position in the ammonia soda industry.

Chapter VII

Ammoniation of Saturated Brine

The saturated brine for soda production is sent to the system generally treated according to one of the methods described in Chapter V. In the soda works the buildings are usually tall so that the brine can be pumped to a head tank, on top of one of the buildings, where it flows down by gravity to various units in the system. The fresh brine from this storage tank is employed first to scrub small quantities of ammonia from the filter gas in the filter washer, from the absorber outlet gas in the absorber weak washer, and from the tower outlet gases in the tower washers (Fig. 23). From this apparatus, the brine, having picked up a
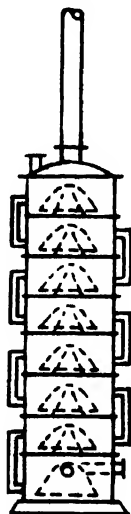
FIG. 23. Tower washer.
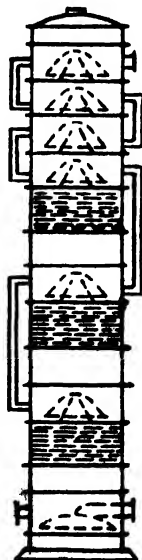
FIG. 24. Absorber

small amount of ammonia and absorbed as much carbon dioxide gas as can be retained by the alkalinity of the slightly ammoniacal solution, flows to the absorber washer and thence to the absorber itself (Fig. 24). From the outlet of one apparatus to the inlet of another a long "U" loop is usually provided in the brine line, to prevent escape of the gases, especially if one unit at one end is working under pressure while the other is under partial vacuum, or if two units are under different vacua.

Theoretically speaking, each leg of these "U" loops need be just so long that the static head of the column of brine will balance the differences of pressure above the brine in the two legs of the loop. Where the brine is flowing down with some velocity, this allowance is generally not sufficient and a longer loop must be allowed to take care of the velocity head.

In the process, the brine is allowed to absorb the desired amount of ammonia prior to its treatment with carbon dioxide in the carbonating towers. This order of treating the brine first with ammonia and then with carbon dioxide is a natural one, for it would be impossible to reverse the order, *i.e.*, to treat the brine first with carbon dioxide and then with ammonia successfully, as carbon dioxide is sparingly soluble in the neutral brine.

Formerly there was a process for distilling the filter liquor and condensing the ammonia vapors to form an ammonia solution of suitable strength in which solid salt was then dissolved to full saturation. Although this insured good saturation of sodium chloride in the resulting ammoniacal brine, the actual operation of the process was attended by considerable mechanical difficulties because of impurities in the salt and loss of ammonia. This procedure was therefore abandoned.

The ammoniation of the brine serves a two-fold purpose. First, it is a means of introducing the required amount of ammonia into the brine, and secondly, it is a means of eliminating the impurities of calcium and magnesium necessary for the production of a high quality soda ash. For, if calcium and magnesium are not eliminated at this stage, they will be precipitated with sodium bicarbonate in the carbonating towers later. The gases that carry ammonia also carry carbon dioxide, whether they come from the filters, from the absorber vacuum system, or from the carbonating towers. Consequently, ammonia dissolved in the brine exists partly also in the form of $(NH_4)_2CO_3$. Hence calcium and magnesium are precipitated in the brine as $CaCO_3$, $MgCO_3$, $MgCO_3 . (NH_4)_2CO_3 . 4H_2O$, $MgCO_3 . NaCl . Na_2CO_3$, and to a small extent basic magnesium carbonate or $Mg(OH)_2$.

1. $Ca^{++} - Salt + (NH_4)_2CO_3 \rightarrow CaCO_3 + (NH_4)_2 - Salt$
2. $Mg^{++} - Salt + (NH_4)_2CO_3 \rightarrow MgCO_3 + (NH_4)_2 - Salt$
3. $MgCO_3 + (NH_4)_2CO_3 + Aq \rightarrow MgCO_3 . (NH_4)_2CO_3 . 4H_2O$
4. $MgCO_3 + NaCl + Na_2CO_3 \rightarrow MgCO_3 . NaCl . Na_2CO_3$
5. $x MgCO_3 + y Mg(OH)_2 \rightarrow (x + y)MgO . x CO_2 . y H_2O$
6. $Mg^{++} - Salt + 2NH_4OH \rightarrow Mg(OH)_2 + (NH_4)_2 - Salt$

However, in the tower washers and weak washers these precipitates of calcium and magnesium carbonates formed in the cold are in a milky suspension so that fortunately little is settled. Most of the precipitate flows with the brine stream to the absorber washer, thence to the absorber and the settling vats, where these impurities ·finally coagulate at a higher temperature.

Besides eliminating calcium and magnesium from the brine, the introduction of ammonia into brine, or the ammoniation with ammonia gas from the distiller has the following effects:

(a) The decrease in solubility of sodium chloride in the resulting brine.

(b) The increase in the volume of the resulting ammoniated brine.

(c) The unavoidable dilution of the saturated brine by steam carried over with the ammonia gas.

(d) The generation of a large quantity of heat of solution of ammonia in the resulting ammoniated brine, heat of partial neutralization of ammonia by CO_2, and heat of condensation from the steam carried over.

These individual factors will be treated more fully below.

(a) **The effect of the decrease in solubility of NaCl.** It is a general rule that a substance which does not react with the solute, or form any complex ion with the solute, commonly decreases the solubility of the solute when the substance is introduced into the same solution. The decrease in the solubility of salt upon the introduction of ammonia is one of the factors that reduced the quantity of sodium bicarbonate which could be formed in the towers due to the decrease in the concentration of sodium chloride in the resulting ammoniated brine.

TABLE 46. Specific Gravity and Concentration of Pure Sodium Chloride Solution at 15° C.

(Based on Gerlach's figures.)

NaCl in Brine Per Cent	Sp. Gr.	NaCl Grams per liter	Chlorine Titer [*]
1	1.0073	10.073	3.447
2	1.0145	20.290	6.492
3	1.0217	30.652	10.488
4	1.0290	41.160	14.084
5	1.0362	51.812	17.729
6	1.0437	62.620	21.427
7	1.0511	73.576	25.174
8	1.0585	84.681	28.976
9	1.0659	95.934	32.826
10	1.0734	107.34	36.730
11	1.0810	118.91	40.688
12	1.0886	130.63	44.698
13	1.0962	142.51	48.763
14	1.1038	154.54	52.880
15	1.1115	166.72	57.048
16	1.1194	179.10	61.284
17	1.1273	191.64	65.575
18	1.1352	204.34	69.920
19	1.1432	217.20	74.320
20	1.1511	230.21	78.773
21	1.1593	243.45	83.302
22	1.1676	256.86	87.892
23	1.1758	270.43	92.536
24	1.1840	284.17	97.236
25	1.1923	298.07	101.99
26	1.2010	312.25	106.84
26.395	1.2043	317.88	108.77

[*] One titer is one-twentieth of one normal.

Table 46 gives the specific gravity and concentration of sodium chloride in C. P. brine, based on Gerlach's figures. With the introduction of
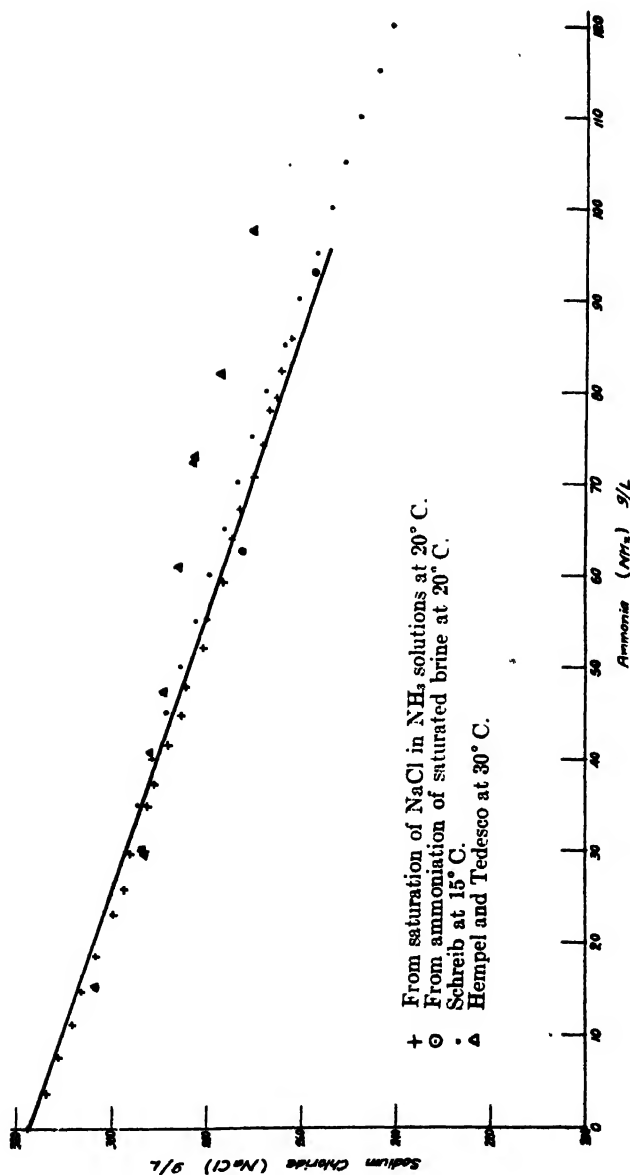
FIG. 25. Curve showing solubility of sodium chloride in aqueous ammonia solutions at 20° C.

+ From saturation of NaCl in NH₃ solutions at 20° C.
⊙ From ammoniation of saturated brine at 20° C.
• Schreib at 15° C.
▲ Hempel and Tedesco at 30° C.

ammonia into the brine, the solubility of sodium chloride in the resulting ammoniacal solution is decreased according to the concentration of ammonia in the brine.

Data on the solubility of sodium chloride in aqueous ammonia solutions seem to be still somewhat in doubt. The original published data were given by Schreib [*] in "vol. %," *i.e.*, in grams NH_3 per 100 cc. of the solution. Schreib admitted that the results were only approximate. The same investigation was conducted by Hempel and Tedesco in 1911 at 30° C.[†] These results we desire to check. We have made the study at 20° C. approaching the equilibria from both directions, *i.e.*, from the solution of sodium chloride in aqueous ammonia solutions and also (for four readings) from the ammoniation of the saturated brine, both at 20° C. The results are given in Tables 47 and 48. For comparison we have also plotted in Schreib's and Hempel and Tedesco's figures (Fig. 25).

Regarding the specific gravity of the resulting ammoniated brine, figures vary considerably. This is due principally to the varying carbon dioxide contents in the ammonia solutions: the higher the concentration of ammonium carbonate in the ammoniated brine, the higher the specific gravity for the same NH_3 and Cl^- titers. High temperatures, of course, lower the specific gravity readings. In our investigation we have taken C. P. ammonia solutions; the specific gravity readings of the resulting solutions will therefore be lower than those of the strong liquors (containing carbon dioxide) in actual plant operation at the same temperature.

A word may be said about the ammonia component in the ammoniated brine. The solubility of ammonia in brine solutions is far greater than is required in operation. Given sufficient cooling, the ammonia titer could easily be brought beyond 110, but it would be quite out of proportion to the sodium chloride concentration, which tends to decrease as the ammonia concentration gets higher. When the ammonia concentration in the brine is made greater, the chlorine titer will necessarily be lowered because of the decrease in solubility of sodium chloride and of the increase in volume in the resulting ammoniated brine. This greatly decreases the concentration of sodium chloride in the liquor. Hence for optimum operating conditions we ammoniate the brine only up to or below 100 titer and do not attempt to push it to the limit of its solubility, because we wish at the same time to maintain the concentration of sodium chloride (*i.e.*, chlorine titer) in the resulting ammoniated brine as high as possible. (See Tables 47 and 48.)

The presence of sodium chloride and of ammonium carbonate tends to raise the specific gravity of the ammonia solution, while ammonia tends to lower it.

If the process is started by introducing into the tower washer or filter washer a cold saturated brine, theoretically some sodium chloride should separate in the absorber during ammoniation. Yet in practice the ammoniated brine from the absorber is generally undersaturated in sodium

[*] *Z. angew. Chem.*, **1888**.
[†] *Ibid.*, **1911**.

TABLE 47. Solubility of Sodium Chloride in Aqueous Ammonia.
(From Saturation of Sodium Chloride in Ammonia Solutions at 20° C.)

Sample No.	Ammonia Solutions				Same Solutions Saturated with C. P. Sodium Chloride						
	Sp. Gr. at 20° C.	NH₃ Titer	NH₃ g./l.	NH₃ Per Cent	Sp. Gr. at 20° C.	NH₃ Titer	Cl⁻ Titer	NH₃ g./l.	NaCl g./l.	NH₃ Per Cent	NaCl Per Cent
1	0.998	4.92	4.18	0.42	1.196	4.52	107.41	3.84	313.93	0.32	26.25
2	0.995	9.86	8.38	0.84	1.192	9.05	106.61	7.69	311.62	0.64	26.14
3	0.993	14.92	12.68	1.28	1.189	13.16	105.49	11.18	308.37	0.94	25.93
4	0.991	19.79	16.82	1.70	1.185	17.48	104.81	14.86	306.32	1.25	25.85
5	0.989	24.65	20.95	2.11	1.182	21.79	103.81	18.52	303.45	1.57	25.67
6	0.988	29.62	25.18	2.55	1.178	27.32	102.60	23.22	299.90	1.97	25.46
7	0.986	34.51	29.33	2.97	1.175	30.43	101.80	25.87	297.53	2.20	25.32
8	0.985	37.06	31.50	3.19	1.173	34.95	101.40	29.71	296.40	2.53	25.27
9	0.982	44.54	37.86	3.84	1.168	41.06	100.20	34.90	292.90	2.92	25.08
10	0.981	49.30	41.90	4.26	1.166	43.79	99.72	37.22	291.48	3.19	25.00
11	0.979	54.23	46.10	4.70	1.164	48.83	98.70	41.50	288.50	3.57	24.79
12	0.977	59.12	50.25	5.12	1.160	52.63	97.80	44.74	285.86	3.86	24.64
13	0.975	64.40	54.74	5.60	1.157	56.33	97.59	47.88	284.96	4.13	24.63
14	0.974	68.85	58.52	6.00	1.152	61.27	96.19	52.08	281.15	4.52	24.41
15	0.972	73.86	62.78	6.45	1.150	64.98	95.99	55.23	280.56	4.80	24.40
16	0.971	77.98	66.28	6.82	1.148	69.49	94.80	59.07	277.10	5.15	24.14
17	0.968	84.42	71.76	7.40	1.146	75.25	94.19	63.96	275.30	5.38	24.02
18	0.967	89.09	75.72	7.83	1.142	78.95	93.59	67.11	273.55	5.88	23.95
19	0.965	93.76	79.70	8.26	1.139	83.06	92.58	70.60	270.60	6.20	23.76
20	0.963	98.39	83.63	8.68	1.136	87.17	91.98	74.09	268.87	6.52	23.67
21	0.962	102.26	86.92	9.04	1.134	91.70	91.38	77.94	267.10	6.82	23.56
22	0.961	103.36	87.86	9.14	1.133	93.29	90.94	79.30	265.88	7.00	23.46
23	0.959	109.38	92.97	9.70	1.132	96.63	90.60	82.14	264.82	7.26	23.40
24	0.958	112.79	95.87	10.01	1.129	100.76	89.93	85.64	262.86	7.59	23.28

TABLE 48. Solubility of Sodium Chloride in Aqueous Ammonia.
(From Ammoniation of Saturated Brine.)

Sp. Gr. at 20° C	NH₁ Titer	Cl⁻ Titer	NH₃ — Grams per liter —	NaCl
1.186	18.09	103.82	15.38	303.46
1.175	35.36	100.60	30.06	294.05
1.147	73.60	93.40	62.56	273.01
1.124	109.38	88.13	92.97	257.60

chloride at the temperature in question due to the following reasons: (1) that the brine has picked up some moisture during the scrubbing of the gases saturated with water vapor at a higher temperature; (2) that in absorbing ammonia gases from the distiller considerable quantities of water are unavoidably introduced into the brine from the steam carried over; and (3) that, to start with, the brine, especially from brine wells, is seldom absolutely saturated. Consequently, the resulting ammoniated brine falls below full saturation with respect to sodium chloride, despite the decrease in solubility of sodium chloride by ammonia. Formerly, an effort was made to increase the concentration of sodium chloride by introducing solid salt into the ammoniated brine after it had left the absorber. As the operation was attended with mechanical difficulties, the practice has been generally discontinued. The increase of concentration of sodium chloride would undoubtedly increase the production of sodium bicarbonate in the towers by its mass action, although the gain may not warrant the trouble.

However, when ammonium chloride is to be recovered from the mother liquor from the columns, it is worth while to fortify the ammoniated brine with pure solid salt to bring the concentration of NaCl to theoretical saturation in the ammoniated brine at the top of the columns, or before the ammoniated brine is sent into the columns for precipitation of NaHCO₃.

(b) **The increase in the volume of brine.** The ammonia gas dissolved in the brine increases its volume just as it increases the volume of water. In the case of pure water, the increase in volume of the aqueous solution of ammonia at 15° C. as shown by the decrease in the specific gravity is given by Lunge and Wiernik in Table 49.

TABLE 49. Specific Gravity of Ammonia Solutions.

Grams NH₃ in 1000 cc Solution at 15° C.	Sp. Gr. 15°/15° C.	Grams NH₃ in 1000 cc. Solution at 15° C	Sp. Gr. 15°/15° C
0	1.000	51.8	0.978
4.5	0.998	56.6	0.976
9.1	0.996	61.4	0.974
13.6	0.994	66.1	0.972
18.2	0.992	70.9	0.970
22.9	0.990	75.7	0.968
27.7	0.988	80.5	0.966
32.5	0.986	85.2	0.964
37.4	0.984	89.9	0.962
42.2	0.982	95.1	0.960
47.0	0.980	100.3	0.958

At a concentration of 80 grams of ammonia per liter, the increase of volume is a little less than 12 per cent. In the case of brine, at the same concentration of ammonia, the volume increase in the resulting ammoniated brine is slightly greater (about 13 per cent), as compared with plain brine of the same sodium chloride concentration. Fortunately, the presence of carbon dioxide in the ammonia gases forming some ammonium carbonate in the ammoniated brine tends to offset this increase in volume.

(c) **The dilution of the saturated brine by steam condensate.** Theoretically it is impossible to get perfectly dry NH_3 gas from the distillers. Production of water vapor can be minimized only by operation at a low temperature, taking advantage of the fact that the aqueous tension of water is much less at a low than at a high temperature (at 50° C. it is only 12 per cent of what it would be at 100° C.). The question is: Can we work at as low a temperature as we desire? In practice, we cannot, because when we cool below about 55° C. the ammonia gases from the distiller containing carbon dioxide, there is a tendency for the solid ammonium carbonate, ammonium carbamate and ammonium bicarbonate crystals to deposit, blocking the gas passage. Equilibrium data from the NH_3-CO_2-H_2O system indicate the possibility of the existence of the following compounds:

> Ammonium Carbonate, $(NH_4)_2CO_3 . H_2O$
> Ammonium Carbamate, $NH_4O . CO . NH_2$
> Ammonium Bicarbonate, NH_4HCO_3
> and the double salts, $NH_4HCO_3 . NH_4O . CO . NH_2$
> and $2NH_4HCO_3 . (NH_4)_2CO_3 . H_2O$

This limitation is a practical one. Following are temperatures at which such substances exist in the solid state at atmospheric pressure.

> Solid $(NH_4)_2CO_3 . H_2O$ exists below 58° C.
> Solid NH_4HCO_3 exists below 60° C.
> Solid $NH_4O . NH_2CO$ exists below 60° C.
> Solid NH_4HS exists at low (unknown) temperature
> Solid $(NH_4)_2S$ exists at low (unknown) temperature

The crystallizing temperature of the ammonia gases varies according to the relative concentration of carbon dioxide the ammonia vapors carry.

Since the pipes are generally large, occasional periods of too low a temperature, if followed promptly by periods of higher temperatures, will clear up the passage by sublimation of the deposited crystals, or the blockade may be broken through by injecting exhaust steam. In such cases of fluctuation, generally considerable steam will be carried over to the absorber with the ammonia gas, diluting the ammoniated brine.

Theoretically at 55° C. and 754 mm. pressure ($\frac{1}{4}''$ vacuum Hg) the partial vapor pressure of steam is 118 mm. Hg., and that of ammonia, hydrogen sulfide, carbon dioxide, and air, therefore, 636 mm. Hg. Of these gases, ammonia and carbon dioxide exist in predominating quantities, and hydrogen sulfide and air may be neglected in our calculations.

In the ammoniated brine obtained the ammonia "titer" (*i.e.*, number of cc. of N H_2SO_4 per 20 cc. of solution) is about 95 (or 80.7 g./l. solution), and CO_2, 500 cc. per 20 cc. (or 49.1 g./l. solution). From this, the ratio of the partial vapor pressure of ammonia to that of carbon dioxide is as 80.7/17 is to 49.1/44 or as 4.75 is to 1.115. Therefore the partial vapor pressure of ammonia is 515 mm. The density of the ammonia vapor at 515 mm. Hg is 0.0395 lb. per cu. ft. and that of water vapor at 118 mm. Hg is 0.00650 lb. per cu. ft. This gives 164.5 grams of steam per 1000 grams of the ammonia distilled over. In this calculation we have assumed that all ammonia and carbon dioxide gases in the ammonia vapors coming over from the distiller have been completely taken up by brine in the absorption system and that the temperature of the ammonia vapors entering the absorber is held at 55° C. constantly. Actually some carbon dioxide gas is left unabsorbed in the spent gas and the temperature of the ammonia vapors from the distiller condensers does fluctuate and rise considerably above 55° C. So in practice from twice to three times the amount of water will go over to the absorber.

In practical absorption operations the 95 ammonia "titer" and 89 chlorine "titer" correspond to 80.7 grams of ammonia and 260 grams of sodium chloride per liter of the ammoniated brine. The Cl⁻ titer of the cold saturated brine was 108, but the brine actually obtained has generally 104-105 Cl⁻ titer. The combined increase in volume due to ammonia absorption and to dilution by the steam condensate in the absorber is therefore 17.6 per cent, of which 4.1 per cent has come from steam carried over by ammonia vapors from the distiller condensers and 13.5 per cent is due to the increase in volume from ammonia absorption, when the ammonia gas from the distiller condensers is maintained at 55° C.

(d) **The generation of heat by the solution of ammonia vapor in the brine and partial neutralization of ammonia by CO_2.** The heat of solution of ammonia gas is 8430 calories per g-mol—a very large quantity. Therefore, to make ammonia gas stay in the brine this quantity of heat must be extracted, *i.e.*, the brine must be cooled during absorption. Water in the brine absorbs ammonia gas with great avidity and there would be no difficulty in preparing an ammonia solution. The whole trouble lies in the ability to cool. Cooling on a large scale is attended with considerable difficulty because of incrustation of the cooling tubes. After ammonia absorption, the impurities in the brine begin to separate in the form of calcium and magnesium carbonates, ferrous sulfide, etc. On striking the cooling tubes these precipitates coagulate and settle on the tubes, in the apparatus, and in the piping system. This crust formation seriously reduces the cooling capacity. Occasionally the entire opening, both in the inlet and outlet of the apparatus and of the pipe, is filled with so much grayish sludge or black scale that no brine can flow through. This may result in the complete interruption of operations.

An approximate estimate of the quantities of heat liberated during absorption follows. This is based on the assumption of a 95 titer of ammonia and 500 cc. of carbon dioxide per 20 cc. of ammoniated brine

and 400 kg. of water vapor per 1000 kg. of ammonia. For every 1000 kg. of ammonia in the absorber, there are 12.4 cubic meters of ammoniated brine made. The specific heat of this ammoniated brine is 0.78 and the specific gravity is 1.175. (The specific gravity varies as the amount of carbon dioxide dissolved in the ammoniated brine.)

(1) Heat of solution of NH_3:

$$\frac{1000}{17} \times 8430 = 496.000 \text{ kg. Cal.}$$

(2) Heat of solution of CO_2:

$$\frac{1000}{80.7} \times 49.1 \times \frac{5880}{44} \text{ (Thomsen) } = 81.500 \text{ kg. Cal.}$$

There is also a large quantity of heat generated from the neutralization of NH_3 by CO_2.

(3) Heat of neutralization of $49.1 \times \dfrac{1000}{80.7}$ kg. of CO_2 by NH_3 by the following reaction:
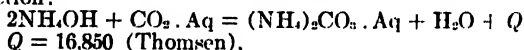
$$2NH_4OH + CO_2 . Aq = (NH_4)_2CO_3 . Aq + H_2O + Q$$
$$Q = 16,850 \text{ (Thomsen)},$$

$$\left(\frac{1000}{80.7} \times \frac{49.1}{44} \times 16,850 \right) = 233.000 \text{ kg. Cal.}$$

(4) Heat from condensation of 400 kg. steam at 55° C. = 400 × 564 = 226.000 kg. Cal.
   Total 496.000 + 81.500 + 233.000 + 226.000 = 1,037,000 kg. Cal.

This quality of heat liberated is sufficient to raise the temperature of the ammoniated brine by

$$\frac{1,037.000}{12.4 \times 1000 \times 1.175 \times .78} = 91.2° \text{ C.}$$

Assuming that the temperature of the brine entering the absorber is 25° C., the amount of heat liberated in it (if not conducted away by the cooling water and radiation) would raise the temperature of the resulting ammoniated brine above its boiling point (91 + 25 = 116° C.). This means that heat is being generated in the absorber at the rate of one-half of one million kilogram calories per ton of ash made, assuming the carbon dioxide titer in the ammoniated brine is 500 cc. per 20 cc. sample.

Consequently, inefficient cooling or an insufficient cooling surface may cause the whole absorber to become hot to the top—a phenomenon known as "hot top." In this condition ammonia gas cannot remain dissolved in the brine in the absorber but passes through to the absorber washer and even to the weak washer; and it may be sent with the exhaust gas to the air through the vacuum pump or "exhauster." This is a source of loss of ammonia which should be watched for. It is the temperature that makes the operation of the absorber the reverse of that of the distiller.

After a preliminary absorption of ammonia gas in the absorber washer and in the upper part of the absorber, the liquor is usually cooled in outside coils of the trombone type (called absorber coolers) made of 8-inch pipes, with return bends over the top tier of which cooling water is

allowed to play and flow down the outside surface of the pipes in thin films. The liquor from the upper part of the absorber enters the bottom tier of these coils and then returns to the bottom of the absorber from the top tier for final absorption. Here the liquor is finally ammoniated to the proper "titer" and flows to the settling vats at a temperature of 60 to 65° C. This temperature range is found suitable for the settling of the precipitate. These settling vats may be some 14 feet in diameter or larger by 25 feet overall height. They are provided with 45° conical bottoms. They may be made of ⅜-inch steel plates, welded or riveted together. Three of such vats are connected in series so as to get the ammoniated brine from the last vat perfectly clear. Each vat is provided with an agitator to keep the precipitate of "mud" loose from the sides and bottoms. The agitators make from 1 r.p.m. in the first vat to 1 revolution per hour in the last vat (outlet vat). A set of three such vats in series has a capacity of from 100 to 250 tons of soda ash every 24 hours, depending upon the quality of brine used. The mud is drawn out regularly from the bottom of each vat by means of a small slow-moving plunger pump, and sent to the distiller to recover ammonia. But before doing this it is best to send the mud to an intermediate settler, called the mud settler, to concentrate the mud further so that as small a volume of mud as possible is sent to the distiller, and the clear ammoniated brine is returned to the system. This is to avoid pumping too large a volume of good brine to the distiller where all the salt it contains is lost. Besides, it would tax the capacity of the distiller unnecessarily. Since the mud so pumped is very thick, it is well to make a branch connection from the filter liquors to the mud pipe so that the mud pump may be flushed and the mud may be diluted by the filter liquor through the pump to the distiller.

The large settling capacity of the vats also helps maintain an ammoniated brine of constant strength for the column operation, making it less susceptible to changes in the concentration of the ammoniated brine made in the absorber.

Normally the heat transfer between a gas and a liquid is not so effective as between a liquid and a liquid. It would seem, therefore, to be more effective to cool the liquor rather than the gas in the absorber by means of cooling tubes. But as the scale formation of mud around the cooling tubes on the liquor side greatly lowers the coefficient of heat transfer, cooling of the liquor alone would not be adequate. In practice, the method of cooling both the liquor and the gases by cooling tubes is employed in the absorber. The liquor cooling surface should have roughly 25 sq. ft. per ton of soda ash, while the gas cooling surface should have 15 sq. ft. per ton of ash, making a total cooling area of 40 sq. ft. per ton of soda ash output. The estimate of cooling surface required, however, depends upon (1) the distribution of cooling area in the apparatus, (2) the temperature of the cooling water available, and (3) the scaling characteristics of the ammoniated brine (*i.e.*, the amount of impurities in the brine). High magnesium brine, such as sea brine, causes the forma-

tion of hard scale which may completely counteract the cooling effect of the liquor cooling system; whereas a high carbon dioxide content in the ammonia gases may cause ammonium carbonate (or bicarbonate) crystals to deposit on the cooling tubes in the gas-cooling system if the temperature drops excessively low. Inasmuch as so many factors are involved, the foregoing figures for cooling area per ton of ash merely afford a rough guide in the design of the absorber.

The absorber and vat house operation is chemically simple but mechanically very troublesome. The plugging of the piping system by the mud incrustation is a serious matter especially when sea salt is used. Duplicate piping systems and cooler sets are employed to facilitate cleaning without interrupting the operation. Tees and crosses are employed in pipe lines and overflow connections to facilitate opening up for cleaning. Tables 50 and 51 give typical analyses of the "mud" from the sea brine pipe main.

TABLE 50. Analysis of Ammoniated Brine Scale, Sample A.
(Hard Scale from Brine Overflow Pipe Using Sea Brine.)

I. Results of analysis		II. Calculated to conventional salts:	
	Per Cent		Per Cent
1. Insoluble matter	0.350	1. Insoluble matter	0.350
2. Fe_2O_3 and Al_2O_3	0.035	2. Fe_2O_3 and Al_2O_3	0.032
3. $S^=$	0.0012	3. FeS	0.003
4. Ca^{++}	2.752	4. $CaCO_3$	6.88
5. Mg^{++}	8.840	5. $MgCO_3$	30.62
6. Na^+	25.357	6. $(NH_4)_2SO_4$	0.019
7. Total ammonia	0.055	7. NH_4HCO_3	0.232
8. Cl^-	12.979	8. NaCl	21.40
9. $SO_4^=$	0.014	9. Na_2CO_3	37.33
10. Total CO_2	36.050	10. $NaHCO_3$	2.63
11. Total alkalinity	16.222	11. H_2O by diff.	0.504

Molecular ratios are:

$$MgCO_3 : \frac{30.62}{84.32} = 0.363 \qquad NaCl : \frac{21.40}{58.45} = 0.366 \qquad Na_2CO_3 : \frac{37.33}{106} = 0.352$$

The molecular ratios of $MgCO_3$, NaCl and Na_2CO_3 are approximately 1:1:1. Hence the triple salt in question should be: $MgCO_3 . Na_2CO_3 . NaCl$. This would correspond to Northupite crystal in natural deposits.

The reasons that tend to prove that the double salt of $CaCO_3$ and Na_2CO_3 (the Gaylussite $CaCO_3 . Na_2CO_3 . 5H_2O$ formation) does not exist here are given below:

(1) That $CaCO_3$ is present in different scale samples in widely varying ratios with respect to Na_2CO_3.

(2) That $CaCO_3$ percentage in each case here is too low to form Gaylussite ($CaCO_3 . Na_2CO_3 . 5H_2O$).

(3) That water present is also far too low to form the hydrated crystals of Gaylussite.

TABLE 51. Analysis of Ammoniated Brine Scale, Sample B.
(Hard Scale from Brine Overflow Pipe Using Sea Brine.)

I. Results of analysis: II. Calculated to conventional salts:

	Per Cent			Per Cent
1. Insoluble matter	0.165		1. Insoluble matter	0.165
2. Fe_2O_3 and Al_2O_3	0.240		2. NaCl	19.152
3. $S^{=}$	0.004		3. Na_2CO_3	34.694
4. Ca^{++}	6.594		4. $NaHCO_3$	0.785
5. Mg^{++}	7.972		5. Na_2SO_4	0.105
6. Na^+	22.838		6. $MgCO_3$	27.637
7. Total ammonia	0.077		7. $CaCO_3$	16.480
8. Cl^-	11.614		8. FeS	0.010
9. $SO_4^{=}$	0.288		9. Fe_2O_3 and Al_2O_3	0.221
10. Total CO_2	36.490		10. $(NH_4)_2SO_4$	0.299
				99.650
			Moisture by difference	0.350
			Total	100.00

Molecular ratios are again:

$$MgCO_3 : \frac{27.637}{84.32} = 0.328 \qquad NaCl : \frac{19.152}{58.45} = 0.328 \qquad Na_2CO_3 : \frac{34.694}{106} = 0.327$$

The molecular ratios of $MgCO_3$, NaCl and Na_2CO_3 are as 1:1:1 and the triple salt in question is again $MgCO_3 . Na_2CO_3 . NaCl$.

These analyses show that the predominating constituents in the scale are $MgCO_3$, Na_2CO_3, NaCl and $CaCO_3$. Several points are noteworthy: (1) magnesium here is not precipitated from ammonia solutions as $Mg(OH)_2$ but in the form of $MgCO_3$ which is normally more soluble than $Mg(OH)_2$; (2) NaCl is present in the mud in excessive quantities, which have been precipitated from an *unsaturated* ammoniated brine (unsaturated with respect to NaCl); and (3) Na_2CO_3 is formed at this stage instead of the far more insoluble $NaHCO_3$. Further study of the composition of the scale confirms the fact that there is a molecular relationship among the three main constituents and that they are in the following molecular ratio:

$$MgCO_3 : NaCl : Na_2CO_3 = 1 : 1 : 1$$

so that NaCl and Na_2CO_3 must have been formed from their respective ionic constituents with $MgCO_3$ in the form of a triple salt $MgCO_3 . NaCl . Na_2CO_3$ in the mud.

The foregoing description applies to brine that has not been treated before ammoniation. If the brine has been pre-treated, no such mud would be formed in large quantities. The loss of NaCl and Na_2CO_3 present in the mud would be avoided and the troublesome operation in the absorber and vat system would be entirely eliminated.

Table 52 gives figures showing the concentrations of magnesium, chlorine, total ammonia, free ammonia, and fixed ammonia at different stages of ammoniation in the absorber system. Certain irregularities, however, are to be noted.

TABLE 52. Composition of Brine at Different Points in the Absorber System During a Certain Period.*

Sample	Magnesium Content Mg./l.	Total Chlorine	Total Ammonia	Free Ammonia	Fixed Ammonia
			Titers		
Fresh brine	1007.7	106.32	nil	nil	nil
Tower washer bottom	154.2	101.50	38.96	35.11	3.85
Absorber washer bottom	117.7	96.69	58.73	54.53	4.20
Pre-settler top	22.70	96.63	66.21	61.48	4.73
Absorber bottom section	19.44	92.10	88.33	84.12	4.21
First vat	13.32	92.28	92.83	87.77	5.06
Intermediate vat	10.50	92.68	91.55	86.50	5.05
Last vat	4.58	91.85	90.60	86.02	4.58
Ammoniated brine storage	4.15	92.48	90.46	87.34	3.12

* Thesis by Dr. W. C. Hsieh with the author.

The preceding analyses were made on the clear portion of each sample. There were 854 mg./l. calcium in the fresh brine sample but only traces in all other samples, showing that calcium is very readily precipitated as $CaCO_3$.

The question of impurities in the sea salt will center upon magnesium because there magnesium exists in larger proportions and also because the

FIG. 26.

Photomicrograph of artificial crystals of ammonium-magnesium carbonate tetrahydrate [$(NH_4)_2CO_3$. $MgCO_3$.$4H_2O$] found in ammoniated brine mud.
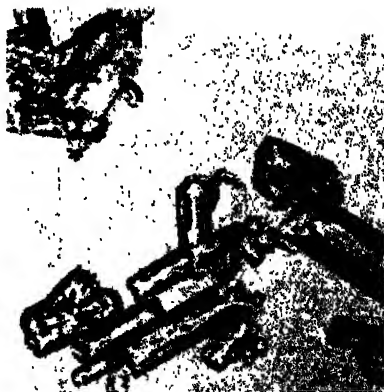
chemistry of magnesium is far more complicated than that of calcium. In the presence of CO_2 in an ammoniacal solution, magnesium seems to have the tendency to precipitate as the carbonate ($MgCO_3$) or at least as a basic carbonate, rather than as the hydroxide [$Mg(OH)_2$], as stated above. Seldom, however, does the magnesium precipitate exist as a simple salt: usually it comes down as a double or triple salt, except where the ammonia and CO_2 gases are weak (such as at the tail end of a washer, where such a simple salt as the magnesium carbonate trihydrate ($MgCO_3$.$3H_2O$) may separate out instead). As the gases become stronger and the brine absorbs more ammonia and CO_2, the double salt of magnesium-ammonium carbonate tetrahydrate ($MgCO_3$. $(NH_4)_2CO_3$.

$4H_2O$) and the triple salt of magnesium-sodium carbonate and sodium chloride ($MgCO_3 . Na_2CO_3 . NaCl$) will occur in place of the simple salt. These salts appear under the microscope at high magnification as in Figs. 26 and 27.* These double and triple salts of magnesium separate most readily at a temperature above 50° C.

Table 53 below reveals the crystal aggregate in the mud at various points starting from the saturated brine to strong liquor at the carbonating tower end.
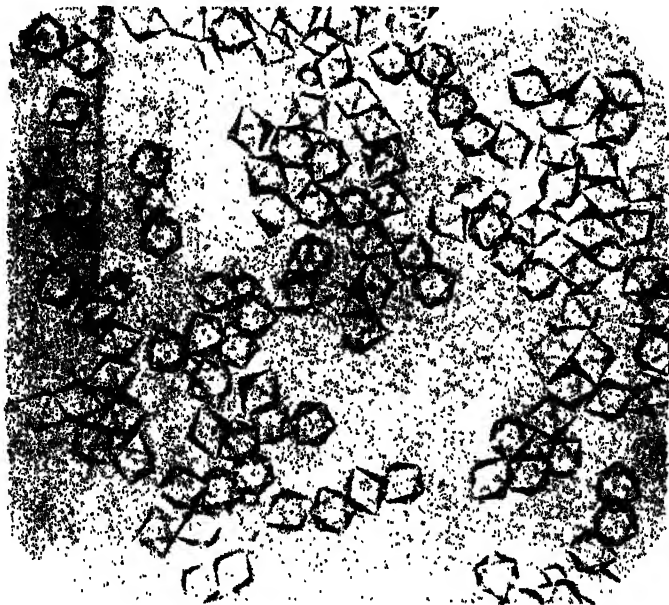
Fig. 27. Photomicrograph of artificial Northupite crystals ($Na_2CO_3 . NaCl . MgCO_3$) found in ammoniated brine mud.

Most of the foregoing crystals are transparent with a wide range of sizes varying from what can be seen at 60-diameter magnification to what cannot be clearly discerned at 800-diameter magnification. They are generally difficult to see at high magnification because of their transparency, but can be seen best at 100-diameter magnification. From the above table it is apparent that at the bottom of absorber washer, absorber, brine cooler and ammoniated brine storage, the triple salt constitutes a large part of the mud formed.

The clear ammoniated brine is cooled to 30° C. in vat liquor coolers similar to the absorber coolers previously described, since hot ammoniated brine, if fed to the top of the columns, would cause excessive vaporization of ammonia by the carbon dioxide spent gases from the

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* Cf. Wilson, E. O., and Chiu, Y. C., "Brine Purification," *Ind. Eng. Chem.*, **26**, 1099 (1934).

TABLE 53. Microscopic Examination of Mud in Ammoniated Brine System.
(From Brine Department to Carbonating Towers.)

No.	Points in System	Character of Crystals	Temp. (° C.)	Relative Proportions
1.	Saturated Brine	Cubic Cryst. (NaCl)	20	Isolated ones only
2.	Weak Washer Bottom Ring	Irr. Cluster Cryst. (Basic MgCO₃)	30	Predominating quantities
		Needle-shaped Cryst. (MgCO₃ . 3H₂O)		Small amount
		Cubic Crystals (NaCl)		Few isolated crystals
3.	Absorber Washer Bottom Ring	Octahedral Cryst. (Triple Salt, MgCO₃ . Na₂CO₃ . NaCl)	45	Large quantities
		Rhombohedral Double Salt (MgCO₃ . (NH₄)₂CO₃ . 4H₂O)		Small amount
		Irr. Cluster Cryst. (Basic MgCO₃)		Small amount
4.	Absorber 5th Ring	Rhombohedral Double Salt (MgCO₃ . (NH₄)₂CO₃ . 4H₂O)	50	Predominating quantities
		Irr. Cluster Cryst. (Basic MgCO₃)		Small amount
		Octahedral Cryst. (Triple Salt)		Small amount
5.	Bottom of Intermediate Settler	Irr. Cluster Cryst. (Basic MgCO₃)	35	Predominating quantities
		Octahedral Cryst. (Triple Salt)		Small amount
		Rhombohedral Cryst. (Double Salt)		Very little (?)
6.	Absorber Bottom	Octahedral Cryst. (Triple Salt)	65	Predominating quantities, (very fine)
		Rhombohedral Cryst. (Double Salt)		Small amount
7.	Vat Bottom	Irr. Cryst. (Basic MgCO₃)	60	Predominating quantities
		Octahedral Cryst. (Triple Salt)		Small amount
		Black Irr. Cryst. (FeS)		Small amount
8.	Brine Cooler Deposit	Octahedral Cryst. (Triple Salt)	35	Exclusively
		Black Irr. Cryst. (FeS)		Isolated particles
9.	Mud at Bottom of Storage Tank	Octahedral Cryst. (Triple Salt)	30	Predominating quantities
		Irr. Black Cluster (FeS)		Small amount
		Rhombohedral Cryst. (Double Salt)		Very little
10.	Sediment in Ammoniated Brine Storage to Towers	Octahedral Cryst. (Triple Salt)	30	Predominating quantities
		Black Irr. Cryst. (FeS)		Small amount
		Rhombohedral Cryst. (Double Salt)		Very little

columns. On cooling the liquor, any magnesium mud, if not completely settled in the vats, would separate in the vat liquor coolers. This causes the formation of hard scale inside the cooling tubes, which obstructs the liquor passage and renders the coolers ineffective. This occurs especially when the temperature of the ammoniated brine is reduced below 30° C. Since the difference in temperature between the ammoniated brine and the cooling water in the vat liquor coolers is smaller than in the absorber coolers, much larger cooling area is required in these vat liquor coolers to get a cool liquor for the column operation. This can be shown mathematically as follows. Suppose in the absorber coolers the ammoniated brine enters the coolers at 60° C. and leaves at 40° C., and in the vat liquor coolers it enters the coolers at 50° C. and leaves at 30° C. Suppose also that the cooling water available has a temperature of 18° C. and its temperature is raised to 25° C. at the outlet in each case, the cooling system in each case being arranged counter-currently. Then the average temperature difference between the liquor and the cooling water in each case is represented by the logarithmic mean

$$\Delta t_{av} = \frac{\Delta t_1 - \Delta t_2}{2.303 \log \dfrac{\Delta t_1}{\Delta t_2}}$$

where Δt_{av} = average temperature difference between the liquor and the cooling water in the cooler.

Δt_1 = temperature difference between the liquor and the cooling water at the liquor entering end.

Δt_2 = temperature difference between the liquor and the cooling water at the liquor leaving end.

Therefore for absorber coolers

$$\Delta t_{av} = \frac{(60 - 25) - (40 - 18)}{2.3 \log \dfrac{60 - 25}{40 - 18}} = 28.0° \text{ C.}$$

For vat liquor coolers

$$\Delta t_{av} = \frac{(50 - 25) - (30 - 18)}{2.3 \log \dfrac{50 - 25}{30 - 18}} = 17.7° \text{ C}$$

so that, other conditions being equal, the cooling surface for the vat liquor coolers must be about 60 per cent larger than that for the absorber coolers. In practice 100 per cent larger area is recommended for the vat liquor coolers.

It is quite important that the ammoniated brine for the column operation should be well settled and free from mud. That good soda ash is made in the absorber and vat system should be kept in mind. For without perfectly clear ammoniated brine, mud would be carried over to the columns, be precipitated with the bicarbonate, and finally find its way to the soda ash, causing a turbid appearance or, in the worst case, a flocculent precipitate in the soda ash solution. This affects the quality of the product of the plant. Furthermore, if mud is accumulated in the columns, cleaning by the usual methods would not be effective and the columns might eventually have to be shut down for a boiling operation and mechanical removal of the scale. The scale would consist mostly of magnesium carbonate, which is difficultly soluble in hot water.

Magnesium mud is most difficult to settle out completely. If the brine used contains large amounts of magnesium with other impurities, magnesium is the last to be removed and small amounts of it will pass through with the brine stream. The amount of magnesium mud left in the ammoniated brine depends upon the settling capacity of the vat system and is determined by the rate of flow *vs.* the volume of the settling vats. With the usual proportion of the height to the diameter (or cross-section area) of the vat construction, it is the volume, rather than the area, of the vat that determines the settling capacity. Table 54 shows the relation of the

TABLE 54.   Rate of Flow vs. Magnesium Carried in the Effluent.*
(Settling Vessel has 23½ cm. × 23½ cm. × 35 cm. Capacity.)

Rate of Flow (cc. per min.)	Mg. Carried in the Ammoniated Brine (gram per liter)	Rate of Flow (cc. per min.)	Mg. Carried in the Ammoniated Brine (gram per liter)
83.3	0.2293	25.0	0.0961
77.0	0.1878	20.0	0.0926
50.0	0.1214	14.3	0.0899
33.3	0.1057	11.1	0.0882

* Thesis by Dr. W. C. Hsieh with the author.

rate of flow *vs.* the amount of magnesium left in the ammoniated brine (sea brine) coming from a settling vessel. These experiments were

carried out with a 5-gal. tin can (23½ × 23½ × 35 cm. high), using normal ammoniated brine from the absorber. Brine enters at the bottom and flows out from the top. The rate of outflow is measured and the magnesium in the effluent determined by analysis. Samples in each case were collected after ten hours of constant flow.
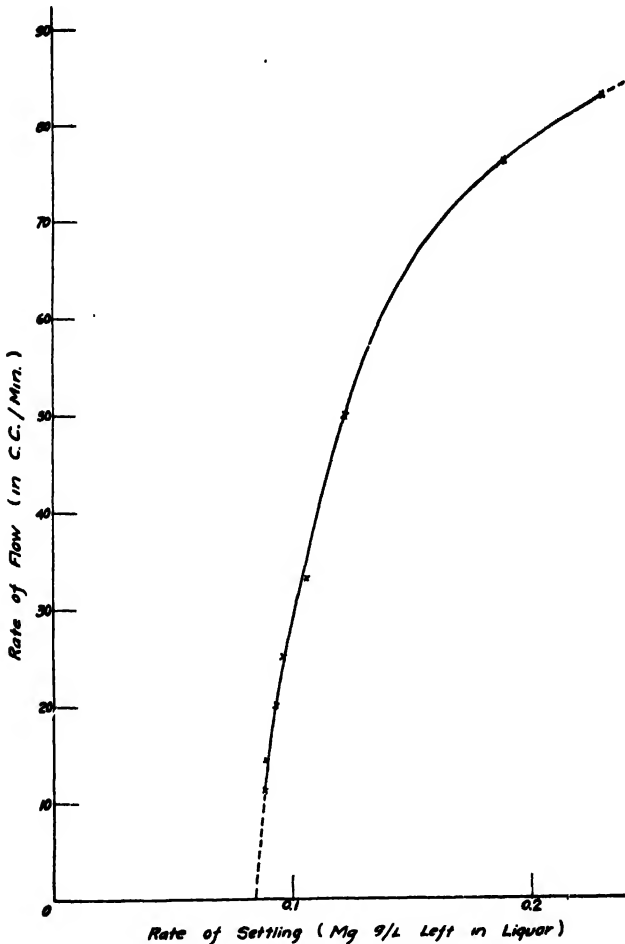
Fig. 28.   Curve showing rate of settling vs. volume of flow.

These results are plotted in a curve (Fig. 28). From this curve it will be seen that for a settling volume of 23.5 × 23.5 × 35 cc., to reduce the magnesium content to within 0.1 milligram per liter in the ammoniated brine, the rate of flow must be below 30 cc. per minute. Granting that this is the highest limit in the green liquor for the column operation, with the usual proportion of the height to the diameter for each of the settling

vats, the minimum volume necessary for settling such brine per ton of soda ash made per 24 hrs. would be 95 cu. ft. for each settling vat.

$$\frac{23.5 \times 23.5 \times 35}{30 \times 60 \times 24} \times 6 \text{ cu. m.} \times 35.3 \text{ cu. ft.} = 95 \text{ cu. ft.}$$

Therefore for a 100-ton plant employing such brine, a minimum of 9500 cu. ft. of settling capacity is needed for the vats. Usually a capacity much in excess of 100 cu. ft. per ton of soda ash made per 24 hrs. must be provided, since allowance must be made for fluctuation of the flow. This indeed calls for a huge settling capacity, and applies to un-pretreated sea salt.

The matter of having a proper ratio of ammonia to sodium chloride in the ammoniated brine is important, for upon this depends the efficiency of the column operation. The Cl⁻ titer (which represents sodium chloride) should be kept as high as possible; but because of dilatation of the volume of brine by ammonia and dilution by the steam condensate as described in the earlier part of the chapter, the sodium chloride concentration in the ammoniated brine is limited by the absorber operating conditions to below 90 Cl⁻ titer. Should the ammoniation in the absorber be carried further, the concentration of sodium chloride (as shown by the Cl⁻ titer) in the ammoniated brine would be greatly reduced. If the ammonia concentration in the brine is too high, excessive amounts of ammonium bicarbonate would also be precipitated together with sodium bicarbonate in the columns. If it is too low, the decomposition of sodium chloride in the columns would be low and too much salt wasted. This affects the rate of salt consumption and the utilization of ammonia and is vitally important to the financial success of the undertaking.

It is found best to have the ratio of 1.08 to 1.12 of NH_3 titer to 1.00 of Cl⁻ titer in the ammoniated brine. Table 55 is based on Hempel and Tedesco's results. It will be noticed that a very high efficiency in the utilization of ammonia is necessarily accompanied by a low efficiency in the utilization of salt, and *vice versa*. The optimum point is reached

TABLE 55. Sodium Chloride and Ammonia Efficiencies for Different Concentrations of NH_3 and NaCl in Ammoniated Brine.*

Grams NH_3 per 100 cc. of Solution	Grams NaCl per 100 cc. of Solution	NH_3:Cl⁻ Titers in Solution	Grams NaHCO₃ in Bicarbonate Obtained per 1000 cc. of Solution	NaCl in Bicarbonate Obtained	NH_4HCO_3 in Bicarbonate Obtained	NaCl Efficiency (decomposition)	NH_3 Efficiency
					Per cent		
18.0	292	21.2 : 99.8	74	0.681	0.40	17.7	83.4
57.9	275	68.1 : 94.0	233	0.033	2.28	59.1	81.4
58.2	273	68.5 : 93.3	234	0.016	2.33	59.8	81.4
63.7	271	75.0 : 92.6	249	0.028	3.53	64.0	79.0
72.4	265	85.1 : 90.6	258	0.037	3.84	67.9	72.3
76.5	260	90.0 : 88.8	269	0.009	4.19	72.1	71.3
82.9	258	97.6 : 88.1	282	0.005	3.91	76.2	68.9
133.3	223	157.0 : 76.3	261	0.014	24.3	82.2	39.7
210.3	195	247.4 : 66.7	249	0.001	69.5	89.6	24.5

* Hempel and Tedesco, *Z. anorg. Chem.*, 24, 2459.

when the utilization of both of these principal raw materials reaches, or is slightly below, 75 per cent, *i.e.*, 99 to 97 for NH_3 titer, and 89 to 90 for Cl^- titer with the ratio 1.10 of NH_3 to 1.00 of Cl. These figures represent the best conditions obtainable in actual plant operation, although theoretically such ammoniated brine is still slightly undersaturated with respect to sodium chloride at this ammonia concentration.

Since in the ammoniating brine, there is a purification effect resulting in the precipitation of $CaCO_3$, $MgCO_3$, $Mg(OH)_2$, etc., in the hot condition, a small amount of NH_3 in the brine exists as NH_4Cl or $(NH_4)_2SO_4$, *i.e.*, as fixed ammonia as mentioned in Chapter V. The amount of the fixed ammonia in the ammoniated brine from the absorber depends upon the purity of the brine used. Generally, the fixed ammonia in the ammoniated brine is from 3 to 5 titer when rock salt brine is used, but it may be as high as 8 to 9 titer when sea salt is used. For the effect of this fixed ammonia on the column reaction, see Chapter V, on the purification of brine. Unless sea brine (which is obtained from sea water directly without crystallization) is used, this would not materially affect the decomposition of NaCl in the columns.

It should be remembered in designing the absorber that the absorption of ammonia requires depth of wash (barbotage). It is not unusual to provide a net depth of 18 to 20 inches in each passette from the serrated edge of the mushroom to the lower edge of the overflow opening.

As has been previously pointed out, if the brine was pre-treated to eliminate calcium and magnesium before it was sent to the system, ammoniation would be exceedingly simple. Most of the difficulties above described would then be avoided. The capacity of the absorber and the vat system would also be considerably increased, and the operating cost greatly lowered. The ammoniation then forms the final step of removing the last traces of impurities in the brine under the best settling conditions, making it possible to produce the highest grade of soda ash.

Chapter VIII

Carbonation of Ammoniated Brine

In early times solutions of salt and ammonium bicarbonate were used in the ammonia soda process. A great step, indeed, was made when ammonia was first employed in the form of a gas to be dissolved in brine and carbon dioxide gas was then introduced into the ammoniacal brine thus formed. This can be readily appreciated when one attempts to precipitate sodium bicarbonate in the laboratory, using brine and ammonium carbonate or bicarbonate solution, even though both these solutions are saturated to start with. From the saturated brine mixed with an equal volume of saturated ammonium bicarbonate in the cold, no immediate precipitate of sodium bicarbonate is obtained. Crystals separate out only after long standing. Sodium bicarbonate in the cold seems to have a great tendency to form supersaturated solutions. On the other hand, granting that both solutions were saturated before they were mixed, the resulting solution is only half saturated in respect to either NaCl or $(NH_4)_2CO_3$ (or NH_4HCO_3). A big advance was made when a method was discovered for introducing ammonia and carbon dioxide both in the form of a gas separately into brine without materially lowering the strength of the brine. The present method of ammoniation with tolerably dry ammonia gas followed by carbonation with carbon dioxide gas is indeed the key to the success of the ammonia soda process. Furthermore, ammoniation is incidentally an important process for the purification of crude brine when the brine has not been pre-treated, while the heat so developed is essential to the separation of calcium and magnesium precipitates from the resulting ammoniated brine. Then again, carbonation with CO_2 gas gives the necessary carbonate and bicarbonate ions in the ammoniated brine, while the heat of neutralization of ammonium hydroxide in the brine by CO_2 (though necessary to be extracted by cooling water towards the bottom of the column) is essential to the formation of good sodium bicarbonate crystals in the columns.

The ammoniated brine from the settling vats should be clear; otherwise the suspended solids would be precipitated with the bicarbonate in the carbonating towers, contaminating the soda ash made. It should be further cooled to about 30° C. in vat coolers, or brine coolers, before being sent to the towers for carbonation; otherwise, because of the increased vapor pressure of ammonia at an elevated temperature, an excessive quantity of ammonia gas that is otherwise available for reaction would be distilled over by the bubbling of CO_2 gases out of the tower into the tower washer, where, on the other hand, more brine would be required to scrub the exit gases free of ammonia before letting them emerge into the

atmosphere. This ℘an be done only within certain limits, because the quantity of fresh brine that can be so employed is limited by the output of soda ash in the plant, *i.e.*, by the quantity of the ammoniated brine made in the absorber at a fixed rate of ammonia distillation. For this
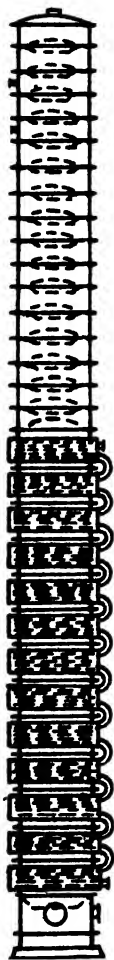
FIG. 29.

Carbonating tower.

reason, some of the older carbonating towers provided the admission of the fresh ammoniated brine, not at the top of the tower but near the middle. This was working on the theory that the free ammonia in the liquor would be converted to ammonium carbonate by CO_2 gas before it could come to the top of the tower, and thus less ammonia would be distilled over by virtue of the lower ammonia vapor-pressure over ammonium carbonate than over free ammonia in the brine. In any case, there is some loss of ammonia in the towers due to gas distillation. This
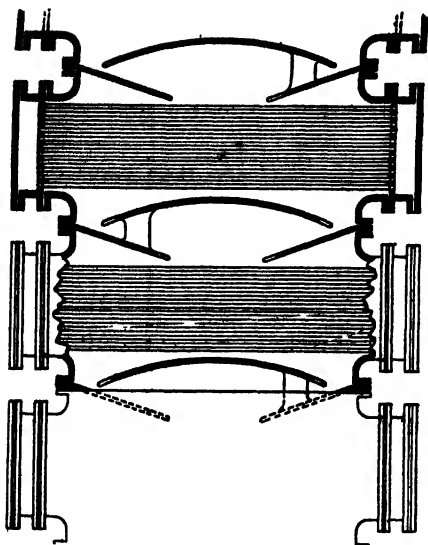
Fig. 30.

Carbonating tower cooling boxes.

is one reason why the ammonia titer in the ammoniated brine should be slightly higher than the chlorine titer.

The clear, cooled, ammoniated brine of proper concentration in sodium chloride and ammonia is treated with CO_2 gas in a carbonating apparatus. There are several types of this apparatus, *e.g.*, Solvay's, Honigmann's,

DETAIL OF MUSHROOM

PLAN

ELEVATION

CARBONATING TOWER
PLAIN RINGS
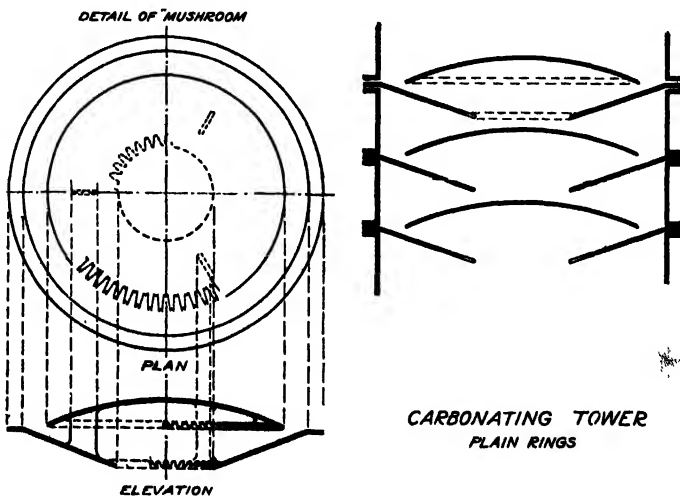
Fig. 31. Carbonating tower upper ring.

Boulouvard's, etc. Among these, Solvay's type is the most universally used (Fig. 29). A tall vertical structure consisting of a number of the mushrooms and division plates, or "passettes," one above the other, is

typical of Solvay's design. The carbonating tower is an example. It consists of cast iron cylindrical sections, or "rings" of about 6 feet or 2 meters inside diameter and 3 feet 4 inches high for each of the bottom cooling sections (Fig. 30) and 18 inches high for each of the upper plain rings (Fig. 31). The cooling system is of the Cogswell type, consisting
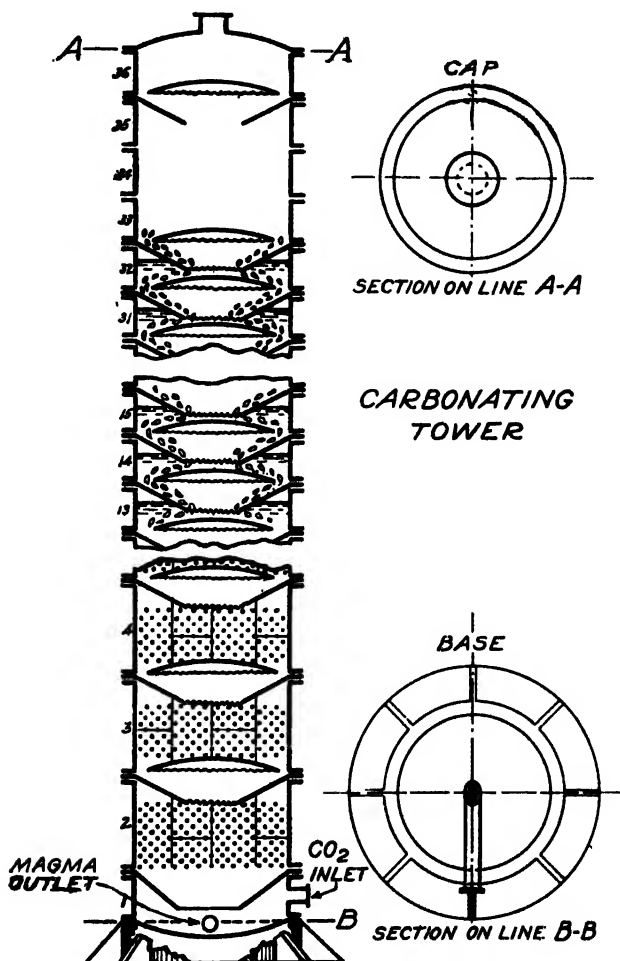
FIG. 32. Carbonating tower or "column."

of a large number of horizontal cast-iron tubes of 2 inches outside diameter, $1\frac{5}{16}$ inches inside diameter, and about 7 feet 3 inches long, laid in rectangular, cast-iron tube sheets. The whole tower is about 75 feet high from the base to the top gas outlet. Carbon dioxide gas enters at the bottom, bubbling up around the edges of an inverted cone opening (**Fig. 32**). The draw opening through which the magma or bicarbonate sludge is drawn out is located at the bottom diametrically opposite the gas outlet.
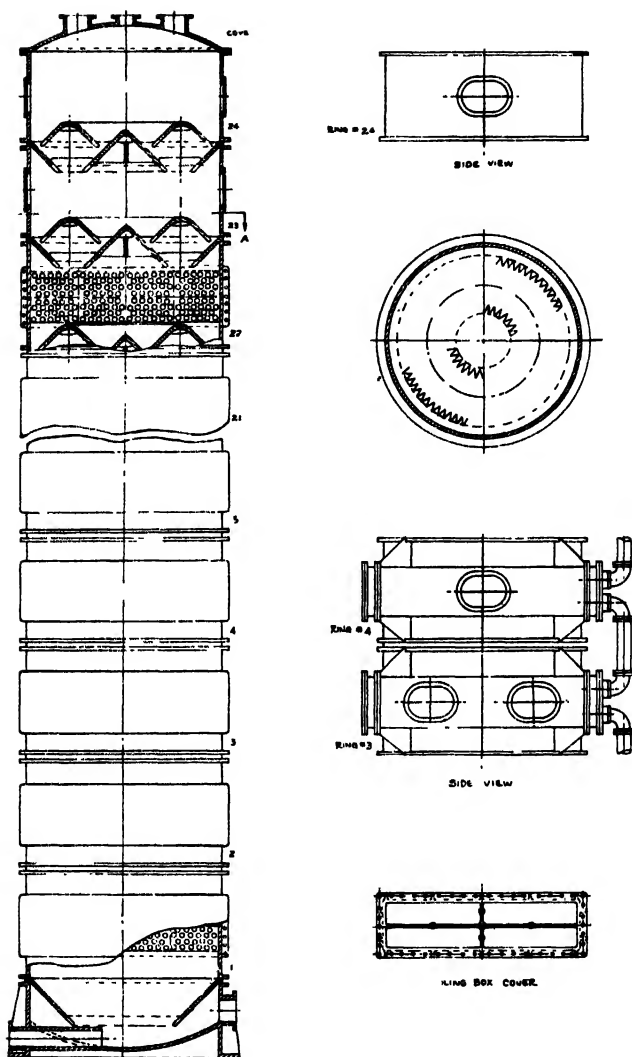
Fig. 33. Another type of carbonating tower.

Instead of working the bicarbonate on the bottom floor, however, the bicarbonate sludge is brought up through a 5-inch draw pipe to a height of 35 to 40 feet by the pressure in the tower itself. It then flows down to the bicarbonate filters located some 35 feet above the bottom floor. This elevation is necessary for vacuum filter working in order to provide a seal by means of a long leg of filter liquor to permit the rise of the liquor column under high vacuum above the level in the storage tanks which are located on the bottom floor, vented to atmosphere.

Within recent decades a departure in the size of the "standard" carbonating tower or "column" has been made. The diameter has been increased from six feet to seven feet six inches for substantially the same height with a large increase in capacity.

Another form of passette construction for the carbonating tower proposed by Mr. E. N. Trump is shown in Fig. 33. This type of passette has a clear passage and is especially good for the precipitating columns, in which fine crystals settle fast and have a tendency to block the passage. The passettes are particularly suitable for the manufacture of refined bicarbonate of soda.

The composition of the normal ammoniated brine to the towers is given in Table 56.

TABLE 56. Composition of Ammoniated Brine.

Sp. gr. (at 30° C.)	1.165–1.175
Free NH_3	97–99 titer
Fixed NH_3	3–5 titer
Chlorine	89–90 titer
Sulfide	0.02 titer
Carbon dioxide	450–500 cc. titer N.T.P.
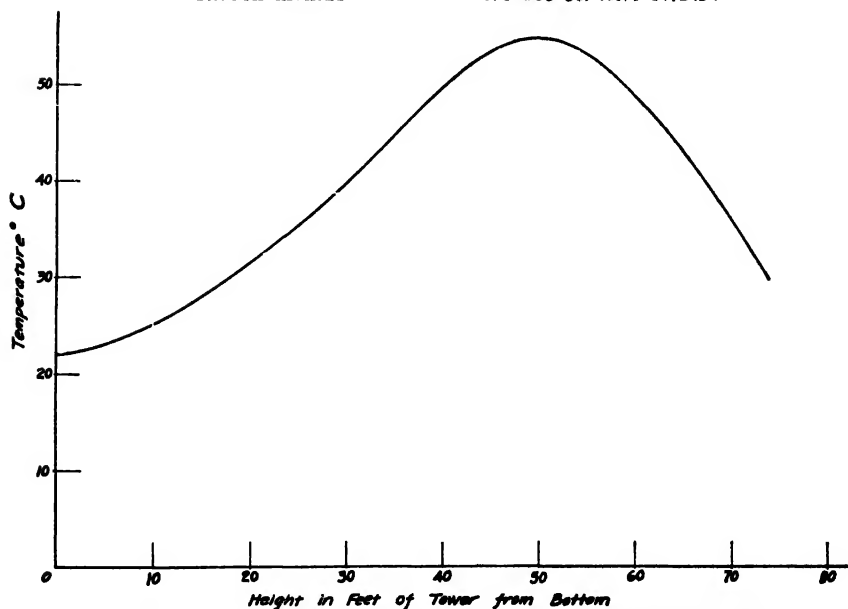
FIG. 34. Approximate temperature gradient in carbonating tower.

In tower operation temperature regulation is very essential. The temperature gradient in the towers should be so graduated by "bleeding" out of the cooling water that the bicarbonate crystals will grow larger and larger toward the bottom as the liquor descends and is cooled. The approximate temperature curve along the height of the tower is shown in Fig. 34.

The lowest temperature is of course to be found at the draw ring at the bottom as the cooling is arranged counter-currently. Various statements appear in textbooks for the best draw liquor temperature, such as 30° C., 32° C., 36° C., etc. Practice does not confirm these statements. With a well-constructed apparatus and good cooling facilities, as low a draw temperature as 22° C. or 20° C. has been found advantageous. It would seem indeed that the temperature for the draw liquor is primarily limited by the cooling capacity with the cooling water available, rather than by the desirability of working at a certain temperature for any chemical reasons. Low draw temperature does not necessarily mean poor crystals or pasty formation of sodium bicarbonate that is hard to filter. The formation of good crystals in the columns depends upon:

(a) High concentrations of ammonia and sodium chloride in the cooled ammoniated brine with a proper ratio between the two titers.

(b) Rich carbon dioxide gas properly cooled.

(c) High reaction temperature at a point about two-thirds of the height of the column above the base.

(d) Gradual cooling from this point down, ending with thorough cooling with as much cooling water as possible as the draw point is reached.

This is consistent with the theory of crystallization. In a solution containing high concentrations of the reacting constituents, sodium chloride, ammonia and carbon dioxide, the ionic concentrations are such that the solubility product of the desired compound is quickly exceeded and the sparingly soluble substance (in this case, sodium bicarbonate) is irreversibly precipitated in a solid form. Then when the reaction occurs at a high temperature, *i.e.*, when the precipitation, as of sodium bicarbonate, takes place in the hot condition, the crystals grow as the liquor is gradually cooled. Finally, cooling the mother liquor to a low temperature for drawing helps to throw as much of the substance out of solution as possible. Thus, a good conversion ratio, "per cent decomposition" and good crystals for filtration and washing operations are simultaneously effected. Furthermore, as the draw liquor is exposed to the air during filtration, the loss of ammonia by exposure is minimized. And further, no strong odor of ammonia gas will cause personal inconvenience to the workmen in the room. By following this procedure the draw temperature can be advantageously brought down as low as can be secured with the cooling water available with no undesirable results.

To get as low a draw temperature as 20° to 22° C. a very low cooling-water temperature is required. It would be impossible to get this draw temperature if surface water or river water were used for cooling during the summer. Underground water, or well water, is best suited for this purpose, as the temperature is always between 15° C. and 16½° C., summer and winter, at a depth of 400 to 450 feet below the surface. This uniform temperature of the cooling water all the year round is desirable,

as uniformity and regularity are required in the ammonia soda industry. The main reaction in the tower is the double decomposition,

$$NH_4HCO_3 + NaCl \leftrightarrows NH_4Cl + NaHCO_3$$
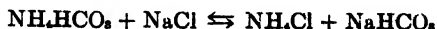
The heat effect is, however, very small as shown below, and the reaction is a typical one of equilibrium.

$$NH_4HCO_3.Aq + NaCl.Aq \leftrightarrows NH_4Cl.Aq + NaHCO_3.Aq + Q_1$$
$$(-199,000) + (-96,600) = (-72,800) + (-222,700) + Q_1$$
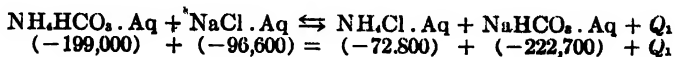
where $Q_1 = -100$ cal. and is the heat of reaction at 15° C. Because of limited accuracy of the heat data available, these figures are evidently beyond the range of significant figures. It seems that the reaction is thermochemically neutral. But when the sparingly soluble sodium bicarbonate (which is still less soluble in the presence of an excess of sodium chloride and ammonium bicarbonate), separates out in a solid form, then there is a positive heat of reaction, which a moment's thought will tell us is nothing but the heat of solution of $NaHCO_3$ crystals. The reaction is then exothermic.

$$NH_4HCO_3.Aq + NaCl.Aq \rightarrow NH_4Cl.Aq + NaHCO_3.Solid + Q_2$$
$$(-199,000) + (-96,600) = (-72,800) + (-227,700) + Q_2$$
$$Q_2 = 4,900 \text{ cal.}$$
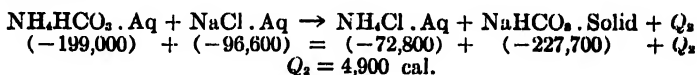
Or per ton of ash, at an average of 72 per cent decomposition, 260 grams per liter of sodium chloride and 6 cubic meters of ammoniated brine,

$$Q_3 = \frac{260 \times 0.72}{58.5} \times 4,900 \text{ cal.} \times 6,000 \text{ l.} = 94,000,000 \text{ cal.}$$

The main heat effect, however, comes from the formation in the liquor of ammonium carbonate from the neutralization of the dissolved ammonia by CO_2 gas. It should be noted that not all this neutralization of the ammonia in the ammoniated brine is effected in the towers, as the ammoniated brine has picked up some carbon dioxide in the absorber system to the extent of about 500 cc. per 20 cc. Assuming 500 cc. of CO_2 per 20 cc. of sample, this leaves 80.7 − 37.9 or 42.8 grams ammonia per liter yet to be neutralized to ammonium carbonate in the towers. Finally all this $(NH_4)_2CO_3$ is converted to acid carbonate, NH_4HCO_3 by further treatment with CO_2 gas in the making towers. The system is unfortunately complicated by the fact that before all the ammonia is neutralized to form normal carbonate, a part of the normal carbonate, $(NH_4)_2CO_3$, formed is immediately hydrolyzed to form NH_4HCO_3 and NH_4OH, so that $(NH_4)_2CO_3$ and NH_4HCO_3 are not formed in distinct stages as described above. Further, ammonia is never 100 per cent bicarbonated to NH_4HCO_3

$$NH_4OH + H_2CO_3 \rightleftarrows NH_4HCO_3 + H_2O \text{ because of hydrolysis.}$$
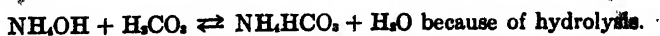
The reaction takes place in this way because it is a salt of a weak acid reacting with a weak base.

$$2NH_4OH + H_2CO_3 \rightleftarrows (NH_4)_2CO_3 + 2H_2O$$
$$+$$
$$H_2O$$
$$\downarrow\uparrow$$
$$NH_4HCO_3 + NH_4OH$$
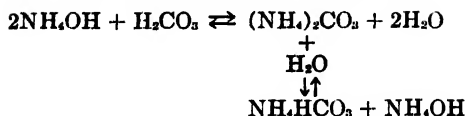
Hence the division of reaction between the cleaning and the making towers is not so distinct as described above.

J. Thomsen gives the heat of neutralization,

$$2NH_3 . Aq + CO_2 . Aq \rightarrow (NH_4)_2CO_3 . Aq + 2H_2O + Q_3$$

$Q_3 = 16,850$ cal. per mol and the heat of solution of CO_2 gas to CO_2 . Aq is 5880 cal. per mol., so that the neutralization of 42.8 grams NH_3 per liter with CO_2 gas to form $(NH_4)_2CO_3$. Aq would cause the evolution of

$$\frac{42.8}{34} \times (16,850 + 5880) = \frac{42.8}{34} \times 22,730 = 28,600 \text{ cal.}$$

or per ton of ash, 28,600 cal. × 6000 l. = 171,600,000 cal.

The second stage

$$(NH_4)_2CO_3 . Aq + H_2CO_3 . Aq \rightarrow 2NH_4HCO_3 . Aq + Q_4,$$
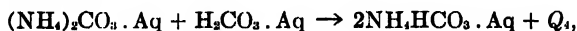
(if the reaction were so definitely marked) gives further heat of reaction

$$(-221,600) + (-168,000) = 2(-199,000) + Q_4$$
$$Q_4 = 8400 \text{ cal. per mol.}$$

The heat of reaction per mol of carbon dioxide due to this reaction then is

$$\frac{80.7}{17} \times \frac{1}{2} \times 8400 = 19,950 \text{ cal}$$

or per ton of ash, 19,950 cal. × 6000 l. = 119,700,000 cal.

To counteract the heat evolved due to the foregoing reaction it is sometimes argued that heat is absorbed because the carbon dioxide expands from $3\frac{1}{3}$ atmospheres (34 to 36 lbs. gage pressure at the inlet) to $1\frac{1}{4}$ atmospheres (3 to 4 lbs. gage pressure at the top of the tower). But this Joule-Thomson heat effect is in reality very small here and need not be taken into account. Hence per ton of ash, the total quantities of heat generated in the cleaning and making towers are:

(1) Heat from carbonation of NH_3 to $(NH_4)_2CO_3$ corresponding to the first stage on the tower side   171,600,000 cal.

(2) Heat from carbonation to $(NH_4)HCO_3$ by CO_2 corresponding to the second stage   119,700,000 cal.

(3) Heat from precipitation of $NaHCO_3$ 94,000,000 cal.

        Total   385,300,000 cal.
per ton of ash
or 385,300 kg. Cal.
per ton of ash

The entire reaction starting from the saturated brine and gaseous ammonia and gaseous carbon dioxide is represented as follows:

$$NaCl \cdot Aq + NH_3 \text{ (gas)} + H_2O \text{ (liquid)} + CO_2 \text{ (gas)} \rightarrow$$
$$NaHCO_3 \text{ (solid)} + NH_4Cl \cdot Aq + Q_6$$
$$(-96,600) + (-12,000) + (-69,000) + (-94,500) = (-227,700) + (-72,800) + Q_6$$
$$Q_6 = 28,400 \text{ cal. per g-mol } NaHCO_3$$
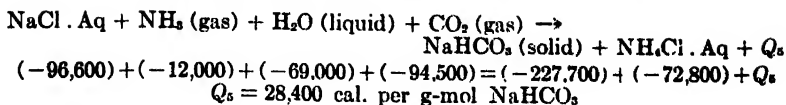
This thermochemical equation represents the total heat effect in the absorbers and in the towers, apart from the heat of condensation of steam carried by the ammonia gases to the absorber. Of this all the heat of solution of ammonia and a part of the heat of neutralization $(2NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O)$ are liberated in the absorber, while the balance is liberated in the towers. The total per ton of ash is

$$\frac{28,400}{53} \times 1,000,000 = 536,000,000 \text{ cal. or } 536,000 \text{ kg. Cal. per ton of ash.}$$

With the heat of condensation of steam $\dfrac{226,000}{12.4} \times 6 = 109,000$ (see p. 121), the total becomes $536,000 + 109,000 = 645,000$ kg. Cal. per ton of ash. This is the theoretical minimum. Actually more ammonia and carbon dioxide are present in the liquor than the quantities called for by the above equation. Hence assuming 75 per cent ammonia efficiency, the minimum value may be put at

$$645,000 \times 1.33 = 860,000 \text{ kg. Cal. per ton of ash.}$$

In the cleaning tower, the heat of carbonation starting with green liquor containing 500 cc. of carbon dioxide per 20 cc. and ending in a precarbonated liquor containing 650 cc. carbon dioxide per 20 cc. is

$$\frac{64 - 49.1}{44} \times \frac{(16,850 + 5880)}{1000} \times \frac{6,000,000}{1000} = 46,100 \text{ kg. Cal. per ton of ash.}$$

In the making tower, the heat liberated by the reaction is:

(a) Heat of carbonation $(171,600 + 119,700 - 46,100) = 245,200$ ⎫ 339,200 kg. Cal.
(b) Heat of crystallization (or solution) of $NaHCO_3 = 94,000$ ⎭ per ton of ash.

The heat generated in the cleaning tower is sufficient to raise its liquor temperature by

$$\frac{46,100}{\left(\dfrac{1.127 + 1.175}{2}\right) \times 0.78 \times 6,000} = 8.5° \text{ C.}$$

$(1.175 = \text{av. specific gravity of the green liquor, } 1.127 = \text{av. specific gravity of the draw liquor, } 0.78 = \text{mean specific heat})$, so that if the green liquor fed to the cleaning tower is at 30° C., the temperature of the precarbonated liquor sent to the making towers will be about 38.5° C. The making towers must then cool the liquor from 38.5° C. to 22° C. (the draw temperature) which requires

$$(38.5 - 22) \times \left(\frac{1.127 + 1.175}{2}\right) \times 0.78 \times 6,000 = 89,000 \text{ kg. Cal. per ton of ash.}$$

Therefore this heat of cooling must be added to the heat of reaction in the making towers above. The total heat which must be extracted by the cooling water in the making towers is then

$$339,200 + 89,000 = 428,200 \text{ kg. Cal. per ton of ash.}$$

It is thus seen that the making towers need intensive cooling while the cleaning towers do not need any cooling at all. But in normal operation, the temperature of the liquor above the cooling section is about 55° C. and it is lowered by the cooling water to about 22° C. at the bottom of the tower.

While the above quantity of heat does not represent any greater quantity of heat to be conducted away than that in the absorber, because of the low temperature to which the draw liquor is to be reduced, the mean temperature difference for the cooling water in the making towers is even less than in the vat coolers. The cooling tubes here are likely to be coated with crystals of $NaHCO_3$ and NH_4HCO_3 so that the coefficient of heat transfer is very small. Consequently, a much larger cooling surface is required in the towers than in the absorber coolers. More than 75 sq. ft. of cooling surface are required in the carbonating tower per ton of soda ash per day, but much depends upon the distribution of the cooling surface in the tower. As many of the cooling tubes as are consistent with the passage of gas and bicarbonate should be concentrated at the bottom sections of the tower. The number of these tubes per section gradually decreases with the height, leaving a very few only on the top sections which are located about half way up in the tower.

It should be remembered that many of the foregoing heat effects were merely calculated and have not been experimentally determined. The results are to be taken as a guide in the absence of experimentally determined data.

In tower operation we are more concerned with the reaction

$$NaCl . Aq + NH_3 . Aq + H_2O + CO_2 \text{ (Gas)} \rightarrow$$
$$NaHCO_3 \text{ (Solid)} + NH_4Cl . Aq + Q_6$$

or,

$$NaCl + NH_4HCO_3 \rightarrow NaHCO_3 + NH_4Cl$$
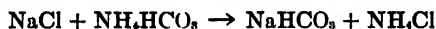
at equilibrium at any given temperature.

$$\frac{[NaHCO_3][NH_4Cl]}{[NaCl][NH_4HCO_3]} = \text{Constant} = K_c$$

where the brackets show molal concentrations of the substances per liter.

For most effective decomposition, K_c should be as high as possible. And for a given K_c at a given temperature the absolute value of the numerator is the larger, the larger the absolute value of the denominator. This means

(1) high molal concentration of NaCl in the ammoniated liquor,
(2) high molal concentration of NH_3 in the ammoniated liquor,
(3) high molal concentration of CO_2 in the tower liquor.

For given concentrations of these substances in solution, the value of the equilibrium constant K_c with respect to the temperature is given by van't Hoff's equation,

$$\frac{d \ln K_e}{dt} = -\frac{Q}{RT^2}$$

where t is the temperature at which the reaction is carried out; T the absolute temperature $= t + 273$; R the perfect gas molal constant $= 1.985$ in cal.; and Q the heat of reaction, which is positive when the heat is evolved in the reaction and negative when absorbed. As Q is positive as shown above (*i.e.*, heat is evolved in the above exothermic reactions), this derivative is negative. That is, K_c is increased, as the temperature is lowered, and *vice versa*. This is in accordance with the LeChatelier principle. Hence,

(4) low draw temperature in the tower.

These four factors are discussed further.

(1) **High concentration of NaCl.** It is apparent from the absorber operation that owing to the increase in volume of brine as the result of ammonia absorption and the decrease in the concentration of sodium chloride as a result of ammoniation as well as the inevitable dilution by steam condensate, the concentration of sodium chloride in the resulting ammoniated brine cannot much exceed 260 grams per liter with an ammonia concentration of about 80 grams per liter. Usually the concentration is between 250 and 260 grams of sodium chloride per liter. The practice of strengthening the liquor by means of solid sodium chloride was attended with some difficulties and has been generally abandoned in modern soda works. For the time being, at least, we must rest contented with a concentration of about 260 grams per liter of sodium chloride in the ammoniated brine.

(2) **High concentration of NH₃.** With good cooling facilities, it is not difficult to get an ammonia concentration higher than 80 grams per liter, while in poorly constructed absorbers with poor cooling arrangements, a phenomenon of "hot top" may be the result. With a limited cooling capacity in the absorber, loss of ammonia through the vacuum pump exhaust is to be watched for, since the absorption of ammonia is simply a matter of cooling. But because of the tendency of the NaCl concentration to decrease in the ammoniated brine as ammoniation is carried further, it is inadvisable to employ an ammonia concentration very much greater than 80 grams per liter. Theoretically, an equivalent strength of ammonia with respect to sodium chloride is all that is required (see equation above). Based on the mass action principle, however, a higher concentration would of course be desirable, but it is found in practice that a very much higher concentration of ammonia greatly reduces the sodium chloride concentration in the resulting ammoniated brine and is not economical in the use of ammonia, because large amounts of free ammonia would be left in the draw liquor. The general practice now is

to employ not more than 12 per cent excess of ammonia over the equivalent amount of sodium chloride (*i.e.*, not over 1.12 equivalent of ammonia for every equivalent of sodium chloride, with about 260 grams of sodium chloride per liter in the ammoniated brine). When a much greater ammonia concentration, say 150 per cent as much as that of sodium chloride, is used, ammonium bicarbonate itself begins to separate in the towers causing cooling difficulties, and considerable ammonium bicarbonate will be formed with the sodium bicarbonate, especially at a low draw temperature. While this does not ultimately contaminate the soda ash, it represents just so much ammonia to be recovered from the dryers, and to be circulated between the towers and the dryers, so the loss of ammonia is proportionately greater. The plugging of the furnace condensers by the formation of ammonium carbonate crystals would also be more likely to occur.

(3) **High concentration of CO_2 gas.** The amount of carbon dioxide dissolved is proportional to the partial pressure of CO_2 gas in contact with the solution. This is Henry's law. It means a high concentration of CO_2 in the gaseous phase, *i.e.*, "rich gas." Theoretically, an equal quantity of CO_2 is recovered from calcination of the bicarbonate in the furnace. As there is always unused CO_2 in the tower waste gas, escaping in the exhaust into the atmosphere and, as is sometimes done, the exhaust gas from the absorber vacuum pump or "exhauster" is allowed to escape into the atmosphere instead of being returned to the carbonating tower, there is a constant loss of CO_2. Consequently, more kiln gas, or "lean gas," must be drawn from the lime kiln. The ratio of the weight of CO_2 in the kiln gas taken to that furnished by the furnace gas is 1.0-1.2 to 1, depending on the rate of the dryer operation relative to the tower operation. Since 42 per cent CO_2 in the kiln gas and 95 per cent CO_2 in the returned gas represent a very good operating result, the percentage of CO_2 in the mixed gases from the carbonating towers cannot average more than 58.2 per cent without pushing the dryer operation beyond the rate of the column operation. When the furnace gas has only 90 per cent CO_2, and the kiln gas 41 per cent, the theoretical percentage of CO_2 in the mixed gas into the column is only 56.3 per cent, when the rate of furnace operation is in step with column operation, *i.e.*, when the furnaces contribute the same amount of CO_2 by weight to the columns as the lime kilns. The volume of the kiln gas taken by the CO_2 compressors is then 2.2 times that of the furnace gas. There is a limit to the CO_2 concentration if the dryer gas is to be mixed with the kiln gas. When the dryer gas is introduced separately as in the double entry arrangement, then the percentage of CO_2 at the bottom gas inlet to the making towers could go up to as high as 90 per cent of CO_2 by volume, if desired.

Fortunately, in Solvay's carbonating towers the gas is forced up through a high column of liquor under a pressure of 34 to 36 lbs. The partial pressure of CO_2 is thus materially increased, giving higher absorption of CO_2 at the bottom of the tower and better utilization of the CO_2 gas. This is a distinct advantage in the Solvay type of carbonator and

the power spent in compressing the gas is well worth while. It is equivalent to introducing richer CO_2 gas for reaction.

The exhaust gas from the absorber system should contain rich CO_2 gas when the absorber system is reasonably air-tight. It should be as high as 60 to 70 per cent CO_2 when there is not much air leakage. It pays to keep the distiller, absorber and vat systems reasonably air-tight to enable this gas to be returned to the towers, not only for the recovery of CO_2 but also of some hydrogen sulfide which is also present in the absorber gas.

(4) **Low draw temperature.** Low temperature at the draw has been said to cause fine crystals of bicarbonate that cannot be filtered dry. This statement is not exactly true. With a high reaction temperature at about the two-thirds point and a proper temperature gradient from that point down, it is unquestionably better to draw the liquor at 22° C., for example, than at 30° C. The decomposition is improved and the loss of ammonia gas by exposure is minimized. This demands a well-distributed and proportioned cooling surface, ample cooling area, a good cooling water, and close regulation of the cooling water course. The bicarbonate crystals will then give a good settling test and can be filtered, washed and calcined without difficulty.

In the course of tower operation, the internal surface and the cooling tubes are gradually coated with bicarbonate crusts, with the result that it is difficult to cool the liquor to the desired draw temperature with a full stream of cooling water. Sometimes also the pressure necessary to force the gas from the CO_2 compressor is materially increased because of the plugging tendency of the nest of cooling tubes by the crystals at the bottom section. But often the pressure *decreases* due to the gas lift effect through the restricted space in the towers. In this connection it may be remarked that never for any length of time should the gases be cut off from any tower while making bicarbonate, or the tower would be plugged solid and serious difficulties ensue. To overcome such difficulties, if the case does happen, steam is injected into the bottom of the tower and into the draw pipe to dissolve out the bicarbonate. When the bicarbonate has set solid at the bottom of the tower, thawing with steam in the draw opening may only open a channel through which the gas would blow through the draw opening and out through the draw pipe. In serious cases the gas comes out thus at the draw opening and the tower must be drawn empty, filled with water and cooked with steam. This always results in off-colored bicarbonate and is at best unsatisfactory. In the normal operation there should be no occasion to resort to such drastic measures. All that is needed would be to cut off the cooling water, change to the lean gas, draw the tower low and thin of bicarbonate, throttle down the CO_2 gas from the compressor, and fill the tower with green liquor. All green liquor is then passed through this cleaning tower to feed making towers. The cooling water is completely cut off to permit the temperature of the liquor to rise to about 39° C. The green liquor tends to dissolve the

bicarbonate crust and the higher temperature drives the reaction backward, unmaking the bicarbonate:

$$NaHCO_3 + NH_4Cl \rightarrow NaCl + NH_4HCO_3 \rightarrow NaCl + NH_3 + CO_2 + H_2O$$

This constitutes the cleaning tower operation and a schedule of about 4 days should be adopted for cleaning the making towers in rotation. The cleaning operation lasts from 18 to 24 hours, depending upon the effectiveness of cleaning (*i.e.*, the temperature of the ammoniated brine and the volume of the green liquor put through). If a tower is over-cleaned or "cleaned to the metal," the bicarbonate made may show a reddish tint and the ash obtained become slightly off-colored. The liquor from the cleaning tower is sent to the making towers by means of CO_2 lift or booster pump. Generally, in cleaning, one tower can best supply carbonated liquor enough to feed 4 making towers.

In the cleaning tower, it is generally considered that the following reaction takes place,

$$2NH_3.Aq + CO_2 (gas) \rightarrow (NH_4)_2CO_3.Aq$$
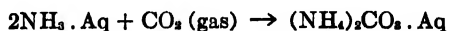
This would mean that with 80.7 grams per liter of ammonia, CO_2 can be present in the carbonated liquor up to $\frac{80.7}{17} \times 22 = 104.4$ grams CO_2 per liter. In practice such a concentration cannot be reached; and before we approach this figure, hydrolysis of ammonium carbonate has set in so far that the concentration of HCO_3^- has attained such a magnitude that $[HCO_3^-] \times [Na^+]$ exceeds the solubility product of $NaHCO_3$ and sodium bicarbonate separates out. Consequently, with the normal strength of ammonia in the ammoniated brine, at no time at any point either in the cleaning or making tower, is there ever in the liquor such a high concentration of CO_2. Generally, crystals begin to show in the carbonated liquor containing more than 80 grams of CO_2 per liter. In actual cleaning operation the liquor is carbonated up to about 64 grams of CO_2 per liter, a figure representing only 61 per cent of the above concentration. All green liquor is cut off from the making towers and it is sent through the cleaning tower as fast as possible to make the cleaning most effective. The precarbonated liquor from this cleaning tower is then fed to all making towers in the group.

In the tower liquor there are present in solution the ionic constituents, Na^+, HCO_3^-, NH_4^+, and Cl^-. There are thus four equilibrium equations, one for each of the four salts, $NaHCO_3$, NH_4Cl, $NaCl$, and NH_4HCO_3, expressing the equilibria between the ions of these salts and their undissociated molecules. Two solubility products for the two least soluble salts, $NaHCO_3$ and NH_4HCO_3, are important. Unfortunately, the exact data on the degree of dissociation (or the activity coefficient) for each of these four salts when present together at high concentrations in solution are not known at present. The solubility of each of these salts when present alone is given in Table 57.

TABLE 57. Solubility of Each Salt in Grams per 100 Cc. Water
When Present Alone.*

Temp. °C.	$NaHCO_3$	NH_4HCO_3	NaCl	NH_4Cl
		—Grams per 100 cc. of Water—		
0	6.90	11.9	35.63	29.4
10	8.15	15.8	35.69	33.3
15	9.03	18.3	35.75(?)	35.2
20	9.60	21.0	35.82	37.2
25	10.35	23.9	35.92	39.3
30	11.10	27.0	36.03	41.4
40	12.70	...	36.32	45.8
50	14.45	...	36.67	50.4
60	16.40	...	37.06	52.2

* For this table and Tables 58 to 60 see A. Seidell's "Solubilities of Inorganic and Organic Substances," New York, D. Van Nostrand Co. These figures are given by Fedotieff, Dibbits and Mulder.

These figures show that sodium bicarbonate is the least soluble of the four. Next comes ammonium bicarbonate and then sodium chloride and ammonium chloride at the temperature of the draw. When, however, the four salts are present together, the salting-out effect of any three salts in solution upon the fourth generally decreases the solubility of each. Then again the common-ion effect materially reduces the solubility of the salts concerned, *e.g.*, $NaHCO_3$ by NaCl and NH_4HCO_3, and NH_4HCO_3 by NH_4Cl. Consequently, $NaHCO_3$ and NH_4HCO_3 are much less soluble in the liquor than when present alone in plain water at the same temperature. The solubilities of $NaHCO_3$ in NaCl solution and in NH_4HCO_3 solution saturated with CO_2 is given by Fedotieff as follows:

TABLE 58. Solubility of $NaHCO_3$ in NaCl Solution Saturated with CO_2.

	At 15° C.			At 30° C.	
		Solubility			Solubility
Sp. Gr.	NaCl	$NaHCO_3$	Sp. Gr.	NaCl	$NaHCO_3$
	Grams/100 cc. Water			Grams/100 cc. Water	
1.056	0.00	8.80	....	....	....
1.063	3.02	6.86	1.066	0.00	11.02
1.073	6.01	5.36	1.079	5.99	7.28
1.096	12.31	3.48	1.100	12.19	4.73
1.127	18.72	2.30	1.127	18.63	3.20
1.158	25.69	1.61	1.156	25.60	2.23
1.203	35.46	1.00	1.199	35.81	1.39

TABLE 59. Solubility of $NaHCO_3$ in NH_4HCO_3 Solution Saturated with CO_2.

	At 15° C.	
	NH_4HCO_3 in Solution	Solubility of $NaHCO_3$
Sp. Gr.	—Grams/100 cc. Water—	
1.056	0.00	8.80
1.061	2.30	8.00
1.065	4.40	7.46
1.073	8.57	6.67
1.090	17.06	5.92

Table 59 shows that the molal decrease by NH_4HCO_3 on the solubility of $NaHCO_3$ is not so much as the molal decrease by NaCl.

Fedotieff also gives the solubility of NH_4HCO_3 in NH_4Cl solutions saturated with CO_2.

TABLE 60. Solubility of NH_4HCO_3 in NH_4Cl Solutions Saturated with CO_2.

Sp. Gr.	At 15° C. NH_4Cl	Solubility of NH_4HCO_3
	Grams/100 cc. Water	
1.064	0.0	18.64
1.063	2.99	16.29
1.062	6.06	14.22
1.062	8.51	12.69
1.065	11.68	11.68
1.069	18.30	9.33
1.076	26.93	7.73
1.085	32.25	6.64
1.085	34.35	6.42

The solubilities of sodium bicarbonate and ammonium bicarbonate in water in the range of the tower operating temperatures (between 22° and 32° C.) have been redetermined by the author. The solubility in each case was determined by taking an excess of C. P. sodium bicarbonate or C. P. ammonium carbonate in 600 cc. water in a tall glass beaker of about one liter capacity, provided with a glass stirrer. The beaker was immersed in an oil bath containing a refined petroleum oil which was circulated by a
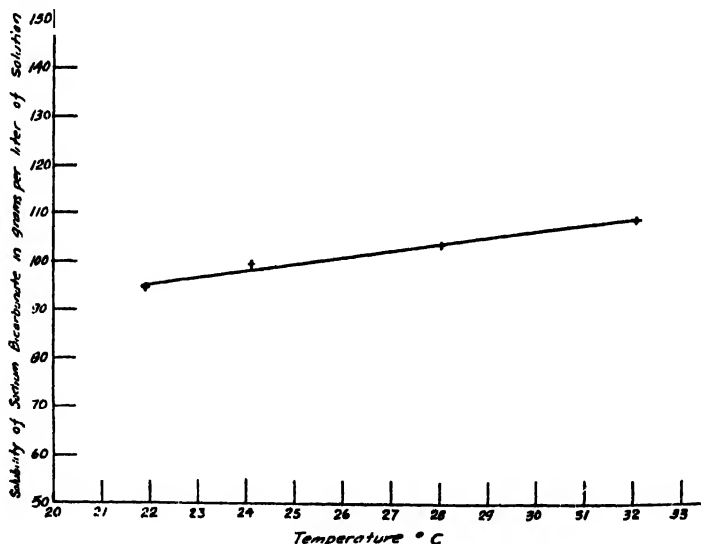
FIG. 35. Curve showing solubility of sodium bicarbonate in water.

pump between the bath and an outside reservoir provided with both electric heating elements and copper cooling water coils for the purposes of heating and cooling respectively. Carbon dioxide gas was bubbled continuously through the suspension in the beaker through a small tubing introduced through a hole in the cover which loosely fitted the mouth of the tall beaker, so that the solution of $NaHCO_3$ or of NH_4HCO_3 was in constant contact with, and kept under the atmosphere of, the CO_2 gas. After the temperature in the beaker had been maintained constant for about

30 minutes with constant stirring, the suspension was allowed to settle for 15 minutes, after which a 20 cc. sample of the clear supernatant liquid was drawn into a 250-cc. volumetric flask and the volume made up to the mark. Ten cc. of the diluted sample was then taken for titration against
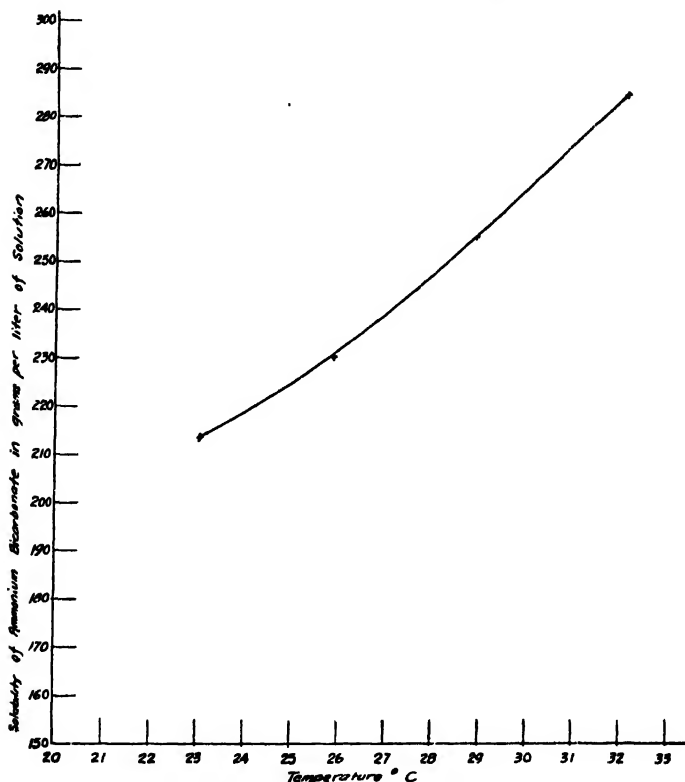
FIG. 36. Curve showing solubility of ammonium bicarbonate in water.

a standard $N/10$ hydrochloric acid solution using methyl orange as the indicator. The results, expressed in grams per liter of the solution, are given in Table 61 (see also Figs. 35 and 36). In the case of ammonium

TABLE 61. Solubilities of Sodium Bicarbonate and Ammonium Bicarbonate in Aqueous Solutions.

Temp. °C.	$NaHCO_3$ Grams/1000 cc. Sol.	Temp. °C.	NH_4HCO_3 Grams/1000 cc. Sol.
21.90	94.4	23.05	213.4
24.10	99.1	25.90	230.5
28.00	103.0	28.90	255.8
32.05	108.2	32.10	286.0

bicarbonate the salt in solution was constantly decomposing, especially at the higher temperatures, so that fine bubbles were evolving from the solution.

In the normal tower liquor after the reaction, there are dissolved in the liquor the quantities of the four salts shown in Table 62.

TABLE 62. Composition of Mother Liquor.
(Sp. gr. 1.126-1.127 at 29.5° C.)

	Grams per Liter of Liquor	
NH$_4$Cl	180–200	
NH$_4$HCO$_3$	90–100	{(all free NH$_3$ calculated to NH$_4$HCO$_3$)
NaCl	70–80	
NaHCO$_3$	6–8	
CO$_2$	40–50	
Sulfide	.010–.020 titer.	

Just how much sodium bicarbonate remains dissolved depends upon the concentrations of the other three salts in the liquor and upon the temperature of the draw. Calculations on the basis of dissociation constants, solubility products, and general mass action laws do not give accurate results in these strong electrolytes at such high concentrations. Bradburn (*Z. angew. Chem.*, p. 82, 1898) gave valuable experimental results for the conditions of operation and the strength of ammoniated brine used in his time. They are given in Table 63.

TABLE 63. Conditions of Carbonating Tower in Operation.

Liquor from Tower Ring No.	Temp. ° C.	NH$_3$ Free Titer	NH$_3$ Total Titer	NH$_4$Cl Grams/liter	NaCl Grams/liter	CO$_2$
Green liquor	34	85.0	89.0	10.7	248.8	67.0
18th ring	40	81.2	89.2	21.4	242.4	77.2
17th "	44	77.4	89.0	31.03	231.0	76.0
16th "	47	71.4	88.3	45.20	221.0	73.3
15th "	48.5	66.0	88.6	60.45	210.0	69.1
14th "	50.5	62.5	89.0	70.88	191.0	65.5
13th "	50.5	58.2	89.0	82.39	188.2	63.0
12th "	49	53.0	89.3	96.83	170.0	59.3
11th "	48	50.0	89.2	104.86	162.2	57.0
10th "	47	46.8	89.0	112.88	150.6	54.0
9th "	46	44.0	89.0	120.37	139.4	52.0
8th "	44.5	40.0	89.0	131.07	131.0	49.0
7th "	42	36.5	89.2	140.97	123.0	47.1
6th "	40	33.3	89.6	150.59	115.0	45.0
5th "	37	30.0	89.6	159.42	105.8	43.3
4th "	33.5	27.0	89.3	167.85	99.7	41.8
3rd "	31	24.7	89.8	174.14	94.0	40.6
2nd "	28.5	23.0	90.0	179.22	88.0	40.0
1st " (Draw)	29	23.0	89.8	178.69	88.3	40.0

The free NH$_3$ titer is lowered if the temperature of the draw liquor is lowered, *i.e.*, if there is sufficient cooling capacity in the tower, and if good regulation is maintained. At a draw temperature of 22° C. the free titer in the draw liquor normally is about 20. The free titer in the draw liquor and its temperature run parallel but will be dependent upon the initial ammonia concentration in the green liquor employed. Low ammonia

liquor may give only 12 to 16 free titers in the draw liquor. Yet the per cent decomposition is low. The amount of CO_2 dissolved ·in the draw liquor depends upon its free ammonia titer.

As has been remarked above and from a table giving the results obtained by Hempel and Tedesco, page 130, it may be shown that a very high NH_3 titer as compared to Cl^- titer, say 157 NH_3 titer : 76 Cl^- titer, causes considerable ammonium bicarbonate to precipitate in the tower with the sodium bicarbonate. The utilization of the available ammonia in the ammoniated brine then is low, *i.e.*, the ratio:

$$\frac{NH_3 \text{ converted to } NH_4Cl \text{ in the tower}}{\text{Total available free } NH_3 \text{ in the } NH_3\text{-brine}}$$

is low, and the handling of ammonia is greater per ton of soda ash made. Consequently, the loss of ammonia is necessarily greater. On the other hand, if the NH_3 titer is low as compared to the Cl^- titer, say the ratio of NH_3 to Cl is less than 1, the utilization of available sodium chloride in the brine is low, *i.e.*, the percentage decomposition is poor. Table 64, based on that given by P. P. Fedotieff (*see* Chapter XII), illustrates this point.

TABLE 64. Efficiencies of Na and NH_3 in Varying Ratios of Cl^- to NH_3 Titers.

Sample No.	Ammoniated Brine Grams/1000 Cc. of Water NaCl	Free NH_3	Ratio Cl^-/NH_3 Titers	Solutions Obtained Equiv. per 1000 cc. Water HCO_3^-	Cl^-	Na	NH_4	Utilization of Na — Per Cent —	Utilization of NH_3
1	479	63.4	1 : 0.456	0.18	8.17	4.62	3.73	43.3	95.1
2	448	77.5	1 : 0.595	0.31	7.65	3.39	4.56	55.7	93.4
3	417	92.7	1 : 0.764	0.51	7.13	2.19	5.45	69.2	90.5
4	397	106.8	1 : 0.925	0.93 ·	6.79	1.44	6.28	78.8	85.1
5	351	96.1	1 : 0.942	0.99	6.00	1.34	5.65	77.7	82.5
6	316	88.6	1 : 0.965	1 07	5.41	1.27	5.21	76.4	79.5
7	294	83.6	1 : 0.978	1.12	5.03	1.23	4.92	75.5	75.1
8	234	70.4	1 : 1.03	1.30	4.00	1.16	4.14	71.0	68.6

It will be seen from Table 64 that there should have been solid sodium chloride in the ammoniated brine in the first five samples. The percentage utilization of sodium chloride is thus decreased when that of ammonia is increased, and *vice versa*. Only Samples Nos. 6 and 7 will give results of any value to actual plant operation.

Table 65 gives average values of the different substances in the normal draw liquor (clear portion).

TABLE 65. Titers in Draw Liquor.

Sp. gr.	1.126–1.127 at 30° C.
Total Cl^-	98–100 titer
Fixed NH_3	72–74 titer
Free NH_3	22–26 titer
CO_2	400–500 cc. per 20 cc. N.T.P.
$S^=$	0.010–0.020 titer

TABLE 66.   Results from Operation of a Highly Ammoniated Brine in an Experimental Column.

Time Min.	Temp. Reaction Ring °C.	Temp. Draw °C.	Draw Titer (Free NH₃)	CO₂ Inlet Per Cent	CO₂ Exit Per Cent	Total NH₃	Fixed NH₃	Total Cl	Sp. Gr. Draw Liquor	CO₂ Diss. Grams per Liter	Conversion Per Cent	NH₃ Efficiency Per Cent
0	22.0	20.0	107.7*	59.5	0.0	108.4	0.7	87.0	1.1207	1.2	...	...
15	24.5	25.0	104.8	60.5	0.2	105.5	0.7	86.9	1.1563	37.8	...	...
30	25.2	22.9	104.8	60.0	0.0	105.3	0.5	87.0	1.1632	44.5	...	...
45	25.7	24.0	103.9	56.8	0.4	104.4	0.5	87.0	1.1771	59.5	...	...
60	25.0	15.0	105.1	55.6	0.5	105.7	0.6	87.6	1.1864	70.4	...	...
75	26.5	19.5	103.0	59.5	1.8	104.2	1.2	89.0	1.1985	82.2	1.4	1.2
90	29.4	24.0	103.3	59.0	3.5	104.2	0.9	87.2	1.2020	95.0	1.0	0.9
105	30.0	21.0	97.8	58.4	4.2	105.0	7.2	88.0	1.1970	91.3	8.18	6.86
120	30.2	21.4	91.3	56.0	5.4	105.8	14.5	88.2	1.1875	82.8	16.44	13.70
135	30.0	20.0	88.0	54.2	25.8	106.1	18.1	89.1	1.1828	81.6	20.3	17.0
150	31.1	22.0	83.1†	70.0	44.5	106.9	23.8	90.1	1.1765	77.0	26.4	22.3
165	31.1	19.0	75.1	62.9	25.2	106.2	31.1	92.0	1.1694	74.6	33.8	29.3
180	31.8	20.6	69.6‡	61.0	35.9	106.6	37.0	92.3	1.1630	72.1	40.1	34.7
195	30.0	18.2	63.2	63.6	42.5	107.0	43.8	92.4	1.1531	68.5	47.5	41.0
210	29.3	22.8	53.6	61.0	48.7	107.0	53.4	92.4	1.1465	65.7	57.8	49.9
225	27.6	18.6	49.6	60.0	51.6	108.5	58.9	93.5	1.1391	63.3	63.0	54.2
240	25.0	21.0	45.4	59.0	55.8	109.0	63.6	93.8	1.1349	59.2	67.8	58.4
255	24.5	20.8	43.3	60.0	55.9	109.0	65.7	93.9	1.1328	58.0	70.0	60.2
285	...	20.0	35.2	56.0	55.3	105.5	70.3	96.0	1.1287	52.1	73.3	66.6
360	...	21.0	33.1	59.4	58.8	106.0	72.9	96.0	1.1275	50.6	76.0	68.7

* This is green liquor sample.
† First ppt. separated from milky suspension.
‡ No new green liquor fed in.

Note.—It is to be observed that in such a small tower operating for such a short duration, the reaction temperature at the two-thirds' point could not possibly rise to such figures as obtain in the plant operation, and the crystals obtained were necessarily poor. Also, it was difficult to effect any temperature regulation in the body of the tower.

It is evident from the Cl⁻ titer in the draw liquor that the liquor volume is here reduced by about 10 per cent, as compared to the ammoniated brine used.

This draw titer (NH₃ titer) depends largely upon the ratio of NH₃ titer to Cl⁻ titer in the green liquor (*i.e.*, the composition of ammoniated brine). When the NH₃ titer is low relative to the Cl titer, a very low draw titer will be obtained. For example, when the NH₃ titer is only **82** and the Cl⁻ titer **91**, a draw of 16 may be obtained. When the NH₃ titer in the green liquor is high, a correspondingly high draw titer will result. For example, when the NH₃ titer is **102** and the Cl titer **89**, a draw titer of **30** will show good decomposition. On the other hand, when the Cl⁻ titer in the green liquor is low (*i.e.*, when brine is too dilute), a high draw titer always ensues. For example, when the Cl titer is **80** or **78** and the NH₃ titer **90**, a draw titer of **40** may be obtained, and the loss of salt will be great.

Table 66 shows an experimental run in a miniature carbonating tower holding a gallon of ammoniated brine, employing as high an ammonia concentration as is practically feasible in actual plant operation. The ammoniated brine (green liquor) had a 107.7 NH₃ titer but the Cl titer obtained was necessarily lowered to 87.0. As refined salt was used in this experiment, only a negligible amount of fixed ammonia was present in the resulting ammoniated brine. It will be seen also that the saturated brine was ammoniated with practically pure ammonia gas and little CO_2 was present in the ammoniated brine. Hence it should be observed that the specific gravity of this ammoniated brine is lower than what it would be under actual plant operating conditions. In the course of carbonation in the experimental tower, the specific gravity increases, reaching a maximum of 1.202, and then decreases as the precipitation of sodium bicarbonate sets in. The specific gravity readings were determined by a pycnometer and so are more accurate than are actually needed. The CO_2 content in the tower liquor also increases in the course of carbonation, reaching a maximum of 95 grams per liter in the highly ammoniated green liquor, representing correspondingly higher values than would obtain in plant operation with normal ammoniated brine. This is also indicated by the high free titer in the draw.

Unless otherwise specified, the figures in Table 66 represent "titers," *i.e.*, the number of cc. of normal solutions per 20-cc. sample.

After 6 hours of carbonation, equilibrium was reached and the "free titer" in the draw reached a constant value. The draw temperature was regulated by the amount of cooling water sent through the cooling sections in this experimental tower. Hence it fluctuated considerably. The average of CO_2 gases used in the carbonation was 59.6 per cent by volume, representing good plant practice, where mixed gases are used.

From the results in Table 66 it will be seen that with an ammonia titer as high as 1.24 times as much as the chlorine titer, keeping the latter at its highest value (87.0 titer), the sodium efficiency obtained (*i.e.*, percentage conversion) was increased only to 76.0 per cent, while the ammo-

nia efficiency was lowered to 68.7 per cent, and this with the mixed gas at about 60 per cent concentration and a low draw temperature of 20° to 21° C.

These results are plotted in Fig. 37, and the curves show that these items are straight-line functions of the fixed ammonia titers in the liquor.

The S^{--} content in the draw liquor shows that there is an excess of sulfide in the system. It is necessary to keep this small excess of sulfide in the tower to ensure the production of white soda ash. The soluble
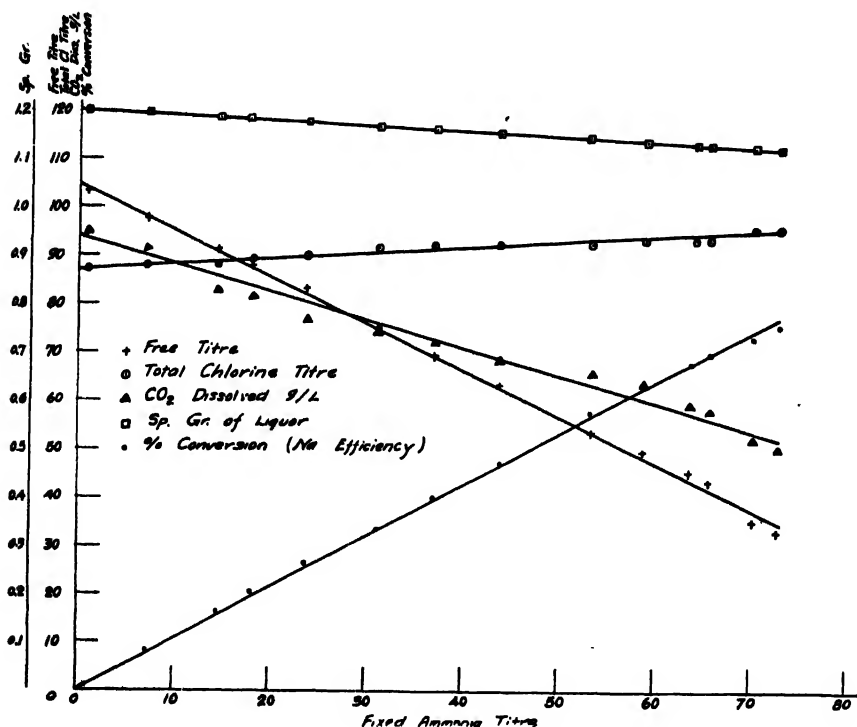
FIG. 37. Curves showing condition in making tower using a highly ammoniated brine.

sulfide in the liquor reacts with the exposed surface of the apparatus and pipes forming a black coating of ferrous sulfide which is not soluble in alkaline solution and so is not attacked by either sodium chloride or CO_2. The sulfide is present naturally in the crude ammonia liquor from the gas works which is the usual source of ammonia supply for alkali plants. In the case of a deficiency of sulfide, sodium sulfide, preferably in a fused form (60%), can be purchased and a solution made from it fed to the still with the filter liquor to compensate for the loss of sulfide from the system. In the towers, some sulfide is oxidized by the air in the CO_2 gases, and some is blown out with the waste gases through the tower

washer into the atmosphere. Hence the necessity of replenishing sulfide in the system to maintain a small excess.

In the cleaning tower, CO_2 in the waste gases should be very small (a fraction of 1 per cent); whereas in the making towers, it runs between 3 and 5 per cent. Sometimes a double gas inlet to the tower, as mentioned above, is provided so that the rich gas from the furnace can be admitted to the bottom of the tower and the best effect of mass action can be obtained. The lean gas is then admitted to the upper gas inlet a few rings above, where the partial pressure of CO_2 in the gas falls to the same value as in the lean gas which is to be admitted there.

The rate of production in the towers and the success of tower operation depend largely upon the richness of CO_2 gases introduced into the towers. This in turn depends upon the percentage of CO_2 in the kiln gas and in the dryer gas. Efforts to secure as rich a CO_2 gas from the lime kilns as possible are well repaid. For every ton of ash there should be delivered to the tower a volume of 800 to 900 cubic meters of the average gas under standard conditions of temperature and pressure. The CO_2 compressors must provide for a piston displacement of 1000 to 1200 cubic meters per ton of ash.

Between the top of the carbonating towers and the tower washer, there is inserted in the gas line a cyclone separator which separates the entrained liquor in the outlet gases and lets it drain back to the top of the towers.

The capacity of a tower depends largely upon the cooling surface. A 6-foot standard tower, about 75 feet high, has a capacity of 50 to 60 metric tons of ash per 24 hours. For a 7½-foot I.D. tower, the capacity is increased to 100-120 tons of soda ash for 24 hours.

The CO_2 compressor in the ammonia soda industry requires some special provisions in its design. In principle it is nothing more or less than a gas pump. But the corrosive character of CO_2 and the dust and ammonia, the gases are likely to carry, make the duty severe. It should meet the following specifications:

(1) The inside of the gas cylinder should have a lining which can be re-bored or renewed when worn.

(2) It should have simple gas valves to insure action because of the corrosive property of CO_2 gas and the presence of some dust in the kiln.

(3) The part in contact with the gas should be all iron owing to the possible presence of some ammonia in the furnace gas.

(4) Ordinary steel cup valves used in the air compressors for gas outlet are rapidly corroded by CO_2 and simple Stainless steel plate valves or heavy rubber disc valves may be used instead. Mechanically operated, plunger-seated steel cup valves of special design, however, have been found very satisfactory. But Stainless steel construction is preferable and resists corrosion much better.

(5) Ordinary lubricating oil in the gas cylinders is affected by CO_2 and becomes sticky. Soda water of about 10 titer strength

injected into the gas cylinders gives clean surfaces and good lubrication.

(6) Besides jacket cooling, water may be injected into the gas outlet pipe. Soda water in large volumes with provisions for circulating and cooling will serve for both lubrication and cooling in the gas cylinders.

Because of low piston speeds (less than 500 f.p.m.) the gas cylinders can tolerate considerable quantities of soda water without knocking; but it is best to locate the discharge valves at the bottom of the gas cylinder, *i.e.*, with top gas intake and bottom discharge.

Between the CO_2 compressors and the tower inlet, the gases pass through a separator so that soda water may not be carried over to the towers. The gas passing from the CO_2 compressors to the columns should be cooled to about 30° C. The column inlet pipe is provided with a tall loop somewhat higher than the tower itself so that liquor from the column cannot run back through the gas pipe, if for any reason the CO_2 compressor is stopped or when the gas delivery fails. The CO_2 compressor for the Solvay tower is the biggest power consumer in the soda plant outside of the main power-generating units.

Lately, some ammonia soda works have installed turbo-compressors for compressing CO_2 gases for carbonation. These compact machines have a very large capacity compared to their size, 15,000 to 25,000 cu. ft. of free gas per min. at a speed of 10,000 to 12,000 r.p.m. It is clearly seen that one such machine can do the work of 5 or 6 piston-type low-speed compressor units (each unit of which may be in itself a duplex machine, having two gas cylinders each delivering gas to a tower). The use of these turbo-compressors results in a great saving in floor space, and also a saving in the first cost. But if the gas volume is small, as in a small alkali plant, the first cost is not low, and the power consumption is even higher. Its drawback is that the gas delivery is not positive, so that if one column is partially plugged and offers greater resistance, little gas is delivered to that column. Also, because of its huge capacity, a large number of columns must be grouped together and run in parallel. This makes the regulation of gases to each individual column rather difficult. As for smaller units with a capacity comparable to that of one unit of the piston-type CO_2 compressor, these turbo-type compressors would be economical neither in first cost nor in maintenance. For large-scale operation, however, these turbo-units offer great possibilities of application.

In one instance, a four-stage turbo-compressor running at 12,500 r.p.m. at 40 lbs. pressure gage and delivering CO_2 gas to a single making tower (1300 cu. ft. per min. piston displacement) requires more than twice as much steam per I.H.P. as would a piston-type compressor for the same service, but the first cost is about the same. At twice this capacity (2600 cu. ft. per min. piston displacement for two making towers), the steam consumption per I.H.P. is still about 80 per cent higher, while the first

cost is cut to a half. At a still higher capacity, however, where one turbo-compressor serves eight making towers, the steam consumption begins to compare favorably with that of the piston-type low-speed compressors, and the first cost is then reduced to a small fraction. This applies to turbo-compressors driven by either single-stage non-condensing turbines or multi-stage bleeder turbines.

At present, the Elliott Company, Ridgway, Pa., the Ingersoll-Rand Company, New York, N. Y., and Allis-Chalmers Mfg. Co., Milwaukee, Wis., are leading in the manufacture of turbo-type compressors in the United States.

The speed of the piston type CO_2 compressors is taken at about 60 to 80 r.p.m., because it is believed that, at this speed, the pulsation effect of the gas delivered to the towers will help keep them open, *i.e.*, the bicarbonate in the towers is not so likely to form incrustations tending to plug them up. But this is just a belief which has grown up in this industry, and lacks scientific background.

Chapter IX

Working of Carbonating Towers or "Columns"

The carbonating towers or "columns" of Solvay design which have about 35 gas-distributing mushrooms, stacked one above the other, separated by plain rings or cooling tube sections, as the case may be, are efficient in gas absorption, but they are very delicate pieces of apparatus when a slurry is involved. In the first place, under no circumstances must the flow of gas entering the tower be interrupted while the tower is full of sodium bicarbonate so as to permit the suspended bicarbonate to settle in the tower. The surging (or pulsation) effect of the carbon dioxide gas delivered from the carbon dioxide compressors is believed to be beneficial in keeping the bicarbonate in the columns in suspension. The flow of gas to the towers will be interrupted either by the failure of the carbon dioxide compressor or, what is more likely to happen and what constitutes a treacherous affair for even an experienced operator, by the failure of one or more of the gas delivery valves to seat properly, so that little or no gas is being delivered to the tower, even though the compressor may be running at its normal speed. Such a case may be diagnosed by the surging up and down of the water levels in the U-shaped manometer located on the suction main. If this condition is allowed to go on undetected for any length of time, the effect will soon begin to show on the tower. Large quantities of sodium bicarbonate crystals will settle in the tower, of which little can be drawn out through the draw line. The only remedy is to introduce steam into the tower bottom. The steam can be introduced best through the steam connections at the sides and through the draw opening in the bottom section. The steam dissolves the bicarbonate, reversing the process according to the following reaction:

$$NaHCO_3 + NH_4Cl \rightarrow NaCl + NH_3 + CO_2 + H_2O$$

and opens its way through the blockade. The introduction of steam must be carefully carried out, or the bicarbonate will show a reddish tint. No more steam should be passed in than is necessary to open up the tower, and the duration of steaming should be as short as possible.

In the second place, even when a tower has been operating smoothly, it needs frequent cleaning. The cooling tubes become coated with precipitated bicarbonate after three or four days' running ("making") and the tower is then said to be getting "dirty." This "dirty" condition is shown by the increase in the percentage of carbon dioxide in the exit gas and in the rise of the draw temperature, since the cooling water is unable to absorb the heat generated in the tower by the chemical reaction because of insulation of the cooling tubes by the bicarbonate scale. The resistance

to gas passage in the tower may have been increased, but in point of fact it is more often attended by a fall, rather than a rise, in the gas pressure through the column. This can be understood when we realize that the space in the tower is decreased by the deposition of large amounts of solid bicarbonate in each section and that the net height of the static column of the liquor is reduced. When the liquor is saturated with carbon dioxide gas, forming a foamy liquid or emulsion, the static head of this emulsified liquor in the tower is also reduced. Such has actually been found to be the case. Only in case of obstruction of the tower bottom by the settling of sodium bicarbonate does the gas pressure increase in the course of operation. The rise in draw temperature is, however, always an infallible indication that the tower needs to be cleaned. In the worst case, the magma at the draw comes out, not in a smooth, continuous stream, but in broken jets, and considerable carbon dioxide gas foam appears in the draw liquor. This shows that the tower is badly plugged and that a channel has been cut in the obstruction in the bottom ring where the draw opening is located, through which the gas finds its way out with the magma. Such a case requires immediate attention.

In a carbonating tower possessing a large number of cooling tubes (hence a large cooling capacity but a limited liquor space), if the exit gas rises excessively on account of a serious shortage of green liquor (or ammoniated brine) or because of the decrease in the rate of draw due to partial plugging of the pipe or of the draw opening, large amounts of bicarbonate accumulate in the tower not only at the bottom but also in the upper cooling sections. If these conditions are allowed to continue, bicarbonate may completely plug the column and the draw stops by itself. When such conditions occur, the best remedy is to shoot in steam momentarily through the draw pipe into the tower bottom. If after repeated application of steam, the tower refuses to be opened up, the only safe way is to turn it to cleaning immediately. This is done by closing off all cooling water, changing over to "lean gas" with gradual bleeding out of the gas, and drawing out the bicarbonate with or without the help of steam at the bottom of the column. In one actual case, because of shortage of green liquor, the exit gas in one making tower rose as high as 45 per cent carbon dioxide, the inlet gas pressure fell from 38 to 30 lbs. per sq. in., the upper tower temperature rose from 55° to 67° C., and the draw became so sluggish that it stopped by itself. The draw liquor became foamy; and after each application of steam, the draw came out in a discontinuous stream and gradually stopped of itself. The ultimate salvation was to turn the tower to cleaning at once. Hence the simultaneous occurrence of an excessive rise in the percentage of carbon dioxide in the exit gas, of a drop in the inlet gas pressure, of a rise of temperature in the upper portion of the tower, and of the appearance of foamy and ever-decreasing volumes of draw liquor indicates that the tower is being badly plugged and that the condition demands immediate attention.

The process of cleaning consists in putting the tower on the lean gas, cutting out the cooling water entirely, bleeding out a portion of the lean

gas, and at the same time drawing the tower hard, until the bicarbonate in the magma is about 8 per cent or less by volume. The normal percentage of bicarbonate by volume after 3 minutes' settling is about 40 to 45 per cent. All the green liquor then is fed to the tower, from the bottom of which this cleaning (precarbonated) liquor is sent to feed the other ("making") towers by means of a booster pump, or better, by means of a carbon dioxide gas lift. The cleaning tower is kept warm (approximately 40° C.) by shutting off the cooling water to help dissolve the deposited bicarbonate therein. By bleeding out the desired portion of the lean gas, the liquor in the cleaning tower is carbonated to just below the precipitating point (65 grams of carbon dioxide per liter). The process of cleaning lasts from 18 to 24 hours. At the end of the cleaning period, the normal process of "making" is resumed, rich gas being turned in and the cooling water admitted about 15 to 20 minutes later. About 5 minutes after the cooling water has been admitted, the tower can be drawn, at first lightly, then in gradually increasing amounts until a normal stream is obtained. The following is an actual sequence of operation when a tower was changed from cleaning to making:

TABLE 67. Interim Conditions of a Column from Cleaning to Making.

10:45 A.M.	Tower changed to making	11:55 A.M.	Draw temp. at 37.0° C
11:00 "	Put on cooling water	12:00 noon	" " " 36.5° C
11:05 "	Draw commences (in a very small stream)	12:05 P.M.	" " " 36.0° C
		12:10 "	" " " 35.5° C
11:10 "	Draw temp. at 46.0° C.	12:20 "	" " " 34.8° C
11:15 "	" " " 44.0° C.	12:30 "	" " " 34.1° C
11:20 "	" " " 42.0° C.	12:40 "	" " " 33.5° C
11:25 "	" " " 41.0° C.	12:50 "	" " " 32.9° C
11:30 "	" " " 40.0° C.	1:00 "	" " " 31.9° C
11:35 "	" " " 39.5° C.	1:20 "	" " " 29.0° C
11:40 "	" " " 39.2° C.	2:10 "	" " " 27.2° C
11:45 "	" " " 38.8° C.	2:40 "	" " " 27.0° C
11:50 "	" " " 38.1° C.		

At 2:40 the draw had been increased to the normal stream. Thus, it takes two to three hours after cooling water has been admitted for the draw to reach its normal temperature. At the start the temperature above the cooling section in the upper portions of the column is 33 to 34° C. and the exit gas contains only 0.8 to 1.0 per cent carbon dioxide. The tower being cold at the start, the grain of the bicarbonate crystals from the tower is necessarily irregular, and the bicarbonate from the filter is wet and difficult to dry. Such bicarbonate needs greater amounts of returned ash for drying. But this does not affect dryer operation, when normal crystals from the other (making) towers are mixed with such bicarbonate in drying. The crystals improve when the tower reaction temperature increases to above 50° C. at about the two-thirds point. When the operation is finally normal, this temperature will be about 60° C.

Experience has shown that a column must be put on cleaning after it has been making for four days (96 hours). This means that with a group of five towers, one tower must be "cleaning" every day, and the

cleaning is done by rotation. With less than four towers, as in very small plants, an equivalent length of time must be adopted for the cleaning period, but the cleaning is less effective because of the small volume of green liquor that can be put through the cleaning tower to feed the making towers. Under these circumstances, it may be necessary to boil the contents of the tower with water and steam once every four to six months. The tower then is first emptied of the bicarbonate and the liquor. It is then filled with water about ¾ full, and steam is introduced at the middle rings as well as the bottom ring of the tower at several points. A small quantity of lean gas is admitted to help agitation, and the circulating pump or gas lift is used to circulate the water in the tower. The temperature of the water in the tower should not be increased above 80° C., as a higher temperature is neither desirable nor necessary. With two or three changes of water in the course of steaming, which lasts for 36 to 48 hours altogether, the entire content will have been practically all dissolved out. All bicarbonates ($NaHCO_3$ and NH_4HCO_3) are dissolved, what is left being small pieces of iron scale (black) and the incrustation of magnesium carbonate (white). Scale in the lower (bottom) portions of the tower normally consists exclusively of sodium bicarbonate, completely soluble in hot water; but the small quantity occurring in the upper portion of the column consists of magnesium carbonate with layers of dark iron scale which is insoluble in hot water, but which may be loosened from the surface by steaming. Such loose pieces must be raked out through manholes or flushed down to the bottom of the tower. It is essential that such pieces be all taken out, for, if they are left in the column, they will form nuclei for scale formation in the column, blocking the draw pipe. For this purpose, as well as for inspection, manholes should be provided diametrically opposite on each side of each ring and of each cooling section of the tower. Because of these cleaning difficulties the minimum number of columns in a plant must be *three*. A maximum number for a group is *five,* one out of five running "on cleaning" every day. This defines the smallest economic unit possible for an ammonia soda plant, and consequently determines the smallest number of units in the plant. This is why the smallest ammonia soda plant that will work efficiently must have a minimum daily output of 100 to 150 tons.

With a group of five columns as a working unit and with the green liquor (ammoniated brine) reasonably free from magnesium, the drastic method described above for cleaning the column by cooking should not be necessary and the usual method of cleaning by running through warm ammoniated brine will suffice. Five columns of standard size should then produce on the average 200 tons of soda ash a day. Larger plants have more than one group of five columns each.

Historically, in the Solvay Process plant, Syracuse, N. Y., the first carbonating towers were 2 meters in diameter and had flat plates with 9-inch holes in the center. These towers were showered with water outside but had no internal cooling. They had a capacity of ten tons of soda ash each per day. Mr. W. B. Cogswell suggested internal cooling, and

nozzles were bolted on several of the rings, through which passed 4-inch tubes carrying cooling water. The capacity was then increased to 20 tons each.

When the second set of towers was built, the lower 8 rings in each tower were provided with 2-inch cast-iron tubes held in the tube sheets with 2-inch lead caulking rings. The division plates, instead of being flat, were made conical and the center holes were increased from 9 inches to 20 inches in diameter. Those center holes were also provided with teeth to subdivide and distribute the gas bubbles in the column.

No steaming or heating of the towers to dissolve the scale from the tubes was found necessary when the columns were properly "cleaned" by running green liquor through them, as mentioned above. These columns were always five in a group, one "cleaning" and four "making." Each day one of the five was put on "cleaning" in rotation. It was reported that in this way each "making" column of 2-meter diameter averaged 60 short tons of soda ash a day.

TABLE 68. Composition of Scale in the Lower Portion of Column.

Analytical Results		Calculated Results	
	Per Cent		Per Cent
NH_3 (free)	1.20	$NaHCO_3$	83.13
$CO_3^=$	3.48	NH_4HCO_3	5.58
HCO_3^-	64.75	Na_2CO_3	5.36
Cl^-	0.34	$NaCl$	0.56
$SO_4^=$	Trace	$CaCO_3$	0.22
Fe_2O_3	Trace	$MgCO_3$	0.42
Ca^{++}	0.09	Water by diff.	4.73
Mg^{++}	0.12		
Na^+	25.30		

The tower draw pipes are also subject to scale formation. Crusts of sodium bicarbonate are formed around the internal walls of the pipes. By a gradual building up of these scales to a thickness of 1 to 2 inches, the pipe opening is gradually reduced, restricting the passage of the draw magma. Frequently these pipes have to be taken down and replaced by new sections of C. I. pipes. Scale is best cleaned out by heating the pipes externally over a small fire or blowing steam through them. Analyses of the scales in the upper and lower portions of a column, respectively, are given in Tables 68 and 69.

Thus it will be seen that the scale in the lower portions of the column, on the internal walls, and around the cooling tubes is practically all sodium bicarbonate, but that that of the upper portion consists also of magnesium carbonate and iron scale.

Magnesium in the tower comes from the mud in the ammoniated brine which has not been completely settled. It is deposited in the upper portions of the tower where the green liquor first strikes the carbon dioxide gas. This is a serious matter. It may be the result of not having sufficient capacity in the settling vats for the quantity of the brine flow, or else it may be due to excessive amounts of magnesium in the brine. As

boiling-out is the most drastic means of cleaning a column, magnesium scale, being difficultly soluble in water, must be removed by hand after the boiling-out operation. As not all rings are provided with ample man-hole area, and not all manholes are so located as to reach every cooling tube or every corner of the column sections, blocking caused by magne-sium scale in the upper cooling sections is detrimental to successful oper-ation of the column. Magnesium mud ($MgCO_3$) in the ammoniated brine is very much more difficult to settle out than calcium mud ($CaCO_3$) as has been mentioned many times elsewhere. The fact that considerable magnesium and no calcium is found in the column scale bears out the

TABLE 69. Composition of Scale in the Upper Portion of Column.

Analytical Results		Calculated Results	
	Per Cent		Per Cent
SiO_2	0.10	$NaHCO_3$	41.30
Fe_2O_3	0.71	Na_2O_3	21.00
$SO_4^=$	0.12	$MgCO_3$	19.39
Cl^-	7.37	$NaCl$	12.15
$S^=$	0.12	NH_4HCO_3	3.90
$CO_3^=$	26.01	$CaCO_3$	0.53
HCO_3^-	33.00	FeS	0.33
NH_3 (free)	0.84	$CaSO_4$	0.61
Ca^{++}	0.39	Fe_2O_3	0.30
Mg^{++}	5.59	SiO_2	0.10
Na^+	25.19	Water by diff.	0.39

truth of this statement. With an effective depth of not less than 15 feet in the vats it is found that a minimum of 6 sq. ft. of settling area is necessary per gallon (U. S.) of liquor flow per minute for an unpretreated sea brine in order to bring the total mud content in the clarified ammo-niated brine to below 0.1 gram per liter.

Following each boiling, an off-color ash is certain to be produced, or an ash yielding a cloudy solution containing considerable insoluble matter. Hence boiling-out or steaming of a column is not to be recommended unless absolutely necessary.

For a good temperature gradient in the tower, the cooling water com-ing out of the uppermost cooling section of the tower should be quite warm and have a temperature of about 45° C. There should not be a sudden chilling of the liquor upon striking the first bank of cooling tubes as it descends from the top. Cooling water entering the bottom section should be as cold as possible but it must be able to take up heat gradu-ally and become warmed to about 45° C. at the top outlet (*i.e.*, from the uppermost cooling section of the tower). The maximum temperature in the tower occurs at about two-thirds of the height from the bottom and is in the neighborhood of 60° C., as stated above.

Table 70 gives the temperature observations in a carbonating tower in operation.

In order that the outlet water leaving the tower may be warm (45° C.), if we start with a very low temperature of the cooling water (16 to 16½° C.) at the bottom, it is evident that there must be a large cooling

TABLE 70. Temperature Gradations in a Tower.

(Unless otherwise mentioned, all temperatures are taken at the outer surface of tower walls.)

	° C.
Green liquor entering Ring 33 (inside wall).........	43.0
Tower exit gas at Ring 36 (inside wall).............	47.0
Surface of Ring 34	48.2
" " " 33	46.6
" " " 32	47.8
" " " 31	47.2
" " " 30	49.2
" " " 29	47.2
" " " 28	51.5
" " " 27	52.3
" " " 26	52.3
" " " 25	52.7
" " " 24	51.8
" " " 23	51.8
" " " 22	53.0
Inside wall of Ring 22	57.0
Surface of Ring 21	52.0
" " " 20	....
" " " 19	49.6
" " " 18	49.6
" " " 17	49.0
" " " 16	49.6
" " " 15	45.6
" " " 14	44.5
" " " 13	44.4
" " " 12	42.0
" " " 11	38.9
" " " 10 (Uppermost cooling section).....	35.8
" " " 9	34.8
" " " 8	34.5
" " " 7	31.6
" " " 6	30.5
" " " 5 (Portion cooling water bled out here)	29.8
" " " 4	28.0
" " " 3	26.9
" " " 2	24.8
" " " 1	22.5
Cooling water entering tower bottom	16.5
" " bled out from mid-cooling section	24.0
" " at exit, topmost cooling section	21.0

surface and a long course of water flow. This is secured by having multiple cooling-water passages in the tower cooling sections and by having a number of these sections, one on top of the other, with a gradually decreasing number of cooling tubes toward the top, the total height of the cooling sections aggregating about one-half of the tower's overall height. Under these conditions, the lower the temperature of the cooling water, the lower will be the draw temperature, and the lower the free ammonia titer in the draw. Consequently, the higher will be the decomposition, with excellent bicarbonate crystals, provided the gas and liquor concentrations are up to normal.

Good bicarbonate crystals should feel gritty or granular between the thumb and the finger, and the layer of bicarbonate on the vacuum drum

filter should be about $\frac{1}{2}$ inch thick at a vacuum of 8 to 10 inches Hg. The free ammonia titer in the draw runs parallel to the draw temperature in the normal rate of draw. For instance, with normal ammoniated brine, when the draw temperature varies from 22 to 40° C. (a very wide range of temperature change) the free titer in the draw follows closely or may be one or two points behind the temperature. This shows how important the draw temperature is and how essential it is to have an ample cooling surface and a cold underground water supply for the cooling medium. With the above cooling arrangement maintaining a high reaction temperature at the two-thirds point in the column, there can be no lower point for the draw temperature, the limit of the draw temperature being the ability of the cooling water to cool and the heat conductivity of the cooling tubes. Using well water having an average temperature of 16 to 16.5° C., it is impossible to cool the draw liquor below 20° C. This at present is the draw temperature limit, unless the cooling water is refrigerated.

The author has actually known of a case where, in the course of years of operation, free sulfur was deposited in the top rings of a column, obstructing the gas passage. This deposit was undoubtedly formed from the oxidation of hydrogen sulfide by the oxygen in the carbon dioxide gas. Thus,

$$2H_2S + O_2 \rightarrow 2H_2O + S_2.$$

Such an excess of oxygen comes from the leakage of air into the furnace gas, which is to a certain extent unavoidable. It has been occasionally observed in the gage glass at the top of the column that the liquor contains suspended free sulfur in the form of a yellowish-white, fine emulsion. The analysis of the free sulfur deposited at the top ring of the column is given in Table 71.

TABLE 71. Analysis of Air-Dried Sample of Deposited Sulfur at the Top of the Column.

	Per Cent
Free sulfur	59.50
NaCl	13.51
NaHCO$_3$	24.11
Na$_2$CO$_3$	1.14
NH$_3$	Trace
Moisture by diff.	1.74

Evidently considerable ammonia had disappeared here and the small amount of sodium carbonate present came from the loss of carbon dioxide in the sodium bicarbonate on exposure to the air.

The capacity of a carbonating tower, like the boiler rating, depends much upon how it is operated. With a given amount of cooling surface (which determines the capacity to a large extent) the quantity of production from a tower depends upon the richness of the CO_2 gases pumped to the tower (also its volume-rate) and the concentration of salt and ammonia in the ammoniated brine fed to the tower, *i.e.*, the Cl⁻ and

free NH_3 titers. A large tower may have very low production when working on a dilute mixed gas or on an ammoniated brine too dilute in chlorine or ammonia. Furthermore, the crystals obtained from columns under such conditions, *i.e.*, with low chlorine titer (weak brine) or with weak mixed gases, or both, are very fine and the soda ash obtained has an abnormally low density (lighter than normal light ash). The one most important factor that determines the capacity of a column is the temperature of the cooling water available.

Chapter X

Filtration of Crude Sodium Bicarbonate (Ammonia Soda): Composition of the Bicarbonate

The crude sodium bicarbonate drawn from the columns is filtered off from the mother liquor. The older type of filter consisted of an open wooden tank with a false bottom, over which was laid a filtering fabric. Mother liquor was sucked from the compartment below the false bottom by means of a piston pump. This inefficient batch filter is now obsolete.

At present, the rotary open-drum filter and the centrifugal filter are the two standard machines. The drum filter has a pipe through the journal at one end, where suction is applied, and a smaller pipe through the journal at the same end or at the other end, where compressed air or waste carbon dioxide gas under pressure from the column exit is introduced. The filtering medium is a woolen felt or blanket wrapped on the drum.

The vacuum helps dry the bicarbonate on the filter and sucks the ammonia gas inward so that ammonia loss to the atmosphere is reduced.

The woolen fabric has a tendency to become plugged by crystals of the bicarbonate, and frequent blowing out with compressed air or carbon dioxide gas is necessary to open the pores. A self-blowing drum filter has one compartment that revolves just past the scraping knife or "doctor"; this compartment is about to enter the liquor, blowing under pressure, while all other compartments are under vacuum. An internal sliding pressure valve connects the opening leading to this compartment with the pressure pipe, so that each compartment is blown once during each revolution. In this way the drum can pick out bicarbonate continuously without stopping for blowing or cleaning. Water in a thin film from a weir is allowed to play on the surface of the bicarbonate to wash the salt (NaCl) from it. The weir box is provided with a standpipe, at the bottom of which is an orifice plate. The standpipe is provided with a gage glass to show the level of water above the orifice plate, feeding the weir box below. Generally, a cold, weak ammonia water from the cooling tower is used for this purpose. Between the weir box and the scraper, or doctor, is provided a number of press rolls made of heavy cast iron (each having about 300 lbs. pressure per foot of length) resting on the surface of the bicarbonate layer, the pressure on the bicarbonate being adjustable. Each press roll serves to level the surface of, and fill any channels in, the bicarbonate layer, and to squeeze out water by its pressure so as to give a drier bicarbonate for furnacing. Because of this crushing action, too, the bicarbonate leaves the scraper in a looser form, free from solid cakes. Each press roll revolves at exactly the same peripheral speed as the

peripheral speed of the bicarbonate on the drum (making allowance for the thickness of the bicarbonate layer). It is independently driven from the same drive of the filter—not merely caused to revolve by the rolling contact with the face of the drum. These pressure rolls, however, have the disadvantage of causing more rapid wearing out of the felt, especially when the edges of the slots on the cylindrical segments of the cage below are not properly rounded off and smoothed. When the bicarbonate crystals are good, the yield (*i.e.*, the weight of sodium carbonate plus sodium chloride obtained per 100 grams of the filtered and washed sodium bicarbonate) should be about 54 grams (*i.e.*, with free moisture about 14 per cent).

The filter drum is a squirrel-cage affair, having slotted segments or cross bars with slots between them. The ends of the drum are closed with covers. It should be all cast iron. Sometimes the cage is covered with cylindrical segments of cast iron or steel plates having a large number of oblique slots. On the face of the slotted drum is wrapped a layer of coarse backing nickel wire cloth or screen which supports a fabric wrapped over it for the filtering medium. This fabric is in the form of a woolen felt or blanket, about $\frac{1}{10}$ inch thick, and is of a loose but uniform texture. Neither the nickel wire cloth nor the woolen blanket stands the corrosion of the mother liquor very well. The life of a woolen blanket for this purpose is about three weeks of continuous service. Ammonia seems to have considerable action on the animal fibers. Yet vegetable fibers like cotton or hemp, which stand the alkaline action of ammonia much better, do not serve the purpose well, because they do not possess the even porosity of woolen felt, and they swell up unevenly and become tight when soaked in the liquor. Consequently, instead of a uniform layer of bicarbonate, there would be uneven spots over the larger pores in the cotton or hemp fabric. Through these pores considerable bicarbonate may pass into the filter liquor and be lost. In place of the nickel wire cloth, a finely fabricated bamboo matting made of small bamboo sticks serves the purpose very well. It lasts longer, and the costly nickel wire cloth can be successfully replaced by the inexpensive, inert bamboo material.

It may not be out of place to dwell somewhat on the early history of the filters introduced into the ammonia soda industry. In the early days of the Solvay Process plant at Syracuse, N. Y., long rectangular filter tanks were used; some of these were 60 feet long by 30 inches wide, and were provided with woven flannel cloths supported on grates at the bottom. In the false bottom below, mother liquor was drawn off by vacuum and the bicarbonate was shovelled out by hand into bottom-dump cars standing alongside. The crystals were washed by means of a swinging perforated pipe. This involved a great deal of labor.

Mr. Ernest Solvay, who was visiting the Syracuse works, suggested to the engineer, Mr. Edward N. Trump, that he devise "a sort of a revolving perforated cylinder with vacuum inside," and the result was the first rotary vacuum filter built by Mr. Trump for the Syracuse plant. Six of

these rotary units replaced all the long, rectangular filter tanks. At first, the scraper knife tended to "glaze" the surface of the blanket so that vacuum had to be taken off every 15 minutes and the blanket washed. The machine was anything but continuous. To avoid "glazing" of the crystals on the blanket, the scraper knife was then attached to the agitator shaft which gave it an oscillating motion, so that the knife would not bear on the same spot during each revolution and form a corrugated surface on the bicarbonate. Later, compressed air was used for blowing back and back-washing. This was a decided improvement, but the filter still had to be stopped for back-washing. A big stride was made when it was found possible to do away with this intermittent operation in back-washing and introduce an automatic self-blowing device. A continuous rotary vacuum filter was developed. The inside of the filter drum was divided into compartments around the circumference, and compressed air was introduced by a valve closing the commutator leading to that particular compartment having just passed over the scraper knife and blowing it when that compartment just entered the liquor again, thus enabling it to pick up a fresh layer of bicarbonate. Then it emerged from the liquor at the back where the cake was washed by a film of water over a weir. The next development was the addition of heavy press-rolls, driven independently at a speed somewhat faster than the peripheral speed of the filter drum itself, to level the bicarbonate layer and squeeze the moisture out of it after it had been washed and before it was scraped off.

The filter thus developed was soon adopted by European Solvay plants as one of the standard pieces of equipiment. From a filter one meter wide and two meters in diameter, it was found possible to obtain enough ammonia soda (crude bicarbonate) to make 120 tons of soda ash a day, using a 10-inch mercury vacuum. Filters were then used also for other service. For ammonia soda service, flannel cloth or felt was used; but for filtering caustic mud, a close-woven rectangular-mesh nickel wire cloth (20×120 mesh or finer) was used in place of the woolen blanket. Narrow grooves supported by internal flanges, or circumferential grooves supported by cross ribs, were milled in the cylinder, and the flannel cloth or nickel wire cloth, as the case might be, was held on the drum by winding it with nickel wire.

These continuous rotary vacuum filters could give a bicarbonate cake containing 12 per cent moisture when good crystals were obtained from the columns. Vertical-suspended, bottom-discharge batch-type centrifugals had been tried in place of these filters, but it was found that the capacity was low, the labor required high, and, above all, the loss of ammonia excessive. A combination of the continuous filter and the centrifuge had been successfully employed. While it did not cause much ammonia loss and did yield a drier bicarbonate, the labor involved was considerable, and the somewhat better yield in the ammonia soda obtained offered no particular advantage in the rotary dryer operation as conducted in present practice.

Continuous rotary vacuum filters are now made in units as large as three meters in diameter and two or more meters long.

The salt content can be reduced but it cannot be entirely eliminated. The "yield" of the bicarbonate (which measures the dryness of the bicarbonate from the filters) is very essential to the successful operation of the soda dryers. Table 72 shows a control analysis of the normal crude bicarbonate from the filter.

TABLE 72. Result of Control Analysis of Filter Bicarbonate.

	Per Cent
(a) Yield	53.52
(b) NaCl	0.36
(c) NH$_3$ (total)	0.92

A complete laboratory analysis on a typical sample is given in Table 73.

TABLE 73. Analysis of Crude Bicarbonate from the Filters.

	Per Cent
NaHCO$_3$	75.60
Na$_2$CO$_3$	6.94
NH$_4$HCO$_3$	3.42
NaCl	0.39
CaCO$_3$	Nil
MgCO$_3$	Trace
Water by diff.	13.65

With the introduction of wash water, the mother liquor is diluted by about 8-10 per cent, *i.e.*, from 6 cubic meters of the liquor per ton of ash the total volume becomes 6.5-6.7 cubic meters. This is found by the
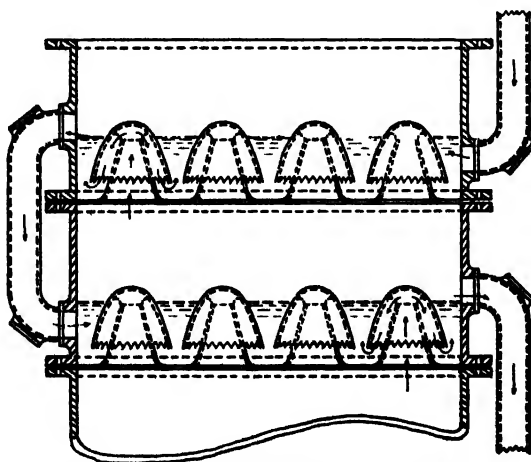
FIG. 38. Multiple passette filter washer.

determination of the chlorine concentrations, Cl⁻ titers, in the liquors entering and leaving the filters. When bicarbonate crystals are poor, more water is consumed in washing out the sodium chloride to the allow-

able limit, and then higher vacuum is required. The loss of bicarbonate through solution by the wash water is estimated normally at 2-4 per cent.

The filter wash water should be a good, soft water. Any hardness in the water will be thrown down as calcium and magnesium carbonates or magnesium hydroxide, plugging the filter blanket. This is a serious matter because it would soon throw the filter out of commission. Generally, one reserve filter is standing by, running empty in water to clean the blanket. Each filter in the battery can be cleaned in this way by rotation. The bicarbonate should not appear dead white but should have a slightly bluish tone, showing a slight excess of sulfide. It should be light and loose, feel like sand between the fingers, and should not produce slimy juice when continually squeezed by forced kneading in the palm of the hand. The bulk specific gravity of the bicarbonate varies with the moisture content and with the crystalline character, *i.e.*, whether it is grainy or pasty. Normally, it should weigh 38 to 42 (average 40) pounds per cubic foot when loosely packed. The vacuum for the drum filter is 8 to 10 inches Hg at the filter. Coarser crystals of bicarbonate require less vacuum than the pasty kind, and the filter takes on a heavier layer of bicarbonate on the blanket—as thick as $\frac{3}{8}$ inch. The coarse crystals also wash better, yielding lower sodium chloride content and drier sodium bicarbonate.

The gases from the filter are drawn through a small washer called the filter washer (Fig. 38) which is similar to the tower washer, but smaller in size and with fewer passettes. The ammonia present in the gases is scrubbed in this filter washer with fresh brine and the brine sent to the tower washer, thence to the absorber washer, and finally to the absorber for making ammoniated brine. The gases are sucked through by means of a vacuum pump, or exhauster, and the exhaust goes to the atmosphere. The volume displacement of the filter exhauster is 120-200 cubic meters per ton of soda ash produced, depending on the crystalline character of the bicarbonate and the size of the filter unit.

The drum filter should have a peripheral speed of 20 to 40 feet per minute. If it runs much faster, the bicarbonate may not filter dry. Too slow a speed, of course, gives a slightly drier product but cuts down the capacity. A self-blowing filter, one meter wide and two meters in diameter, today has a capacity of 150-200 tons of ash per 24 hours working on a good bicarbonate. A small filter, 30 inches wide and 4 feet in diameter, has a capacity of 80-100 tons of ash per 24 hours. The capacity of the filter is largely dependent upon the crystalline character of the bicarbonate. A filter turning out 80 tons of ash on coarse-grained bicarbonate may work with great difficulty on a pasty bicarbonate at the rate of only 45 tons per 24 hours.

The filter operation is important because a difference of a few per cent in the moisture content, measured as the "yield" of the bicarbonate, makes a great difference in the behavior of the bicarbonate in the drying operation.

The composition of crude sodium bicarbonate has been carefully studied and the results of analyses are given in Table 74.

TABLE 74. Complete Analysis of Bicarbonate from Filter.

(Sample granular to the feel. Setting test 3 minutes to a clear solution with sharp solid sludge boundary.)

Per Cent

1. Analytical Results:

	Per Cent
NH_3 (total)	0.74
$CO_3^=$	4.52
HCO_3^-	53.02
Cl^-	0.16
$SO_4^=$	0.07
Fe_2O_3	Trace
Ca^{++}	Trace
Mg^{++}	0.05
Na^+	22.18

2. Calculated Results:

$NaHCO_3$	69.28
Na_2CO_3	7.76
NH_4HCO_3	3.45
$NaCl$	0.26
$MgCO_3$	0.17
Na_2SO_4	0.10
H_2O by diff.	18.98

The small amount of NH_4Cl has been neglected.

3. Confirmatory Checks on Results:

A. Yield by weighing residue on ignition:

a. Residue on ignition		52.00
b. Residue from $NaHCO_3$, $69.28 \times \dfrac{53}{84}$	43.72	
" Na_2CO_3	7.76	
" $NaCl$	0.26	
" Na_2SO_4	0.10	
" $MgCO_3$	0.17	
Total		52.01

B. Total losses on ignition:

a. Total loss on ignition (expt.)		48.00
b. Total loss on ignition (calc.)		
From H_2O	18.98	
" $NaHCO_3$, 69.28×0.369	25.56	
" NH_4HCO_3	3.45	
Total		47.99

C. Yield by titration using methyl orange:

a. Na_2CO_3 yield (expt.)		51.74
b. Na_2CO_3 yield (calc.) from Na_2CO_3	7.76	
From $NaHCO_3$, 69.28×0.631	43.72	
" $MgCO_3$ as Na_2CO_3 $0.17 \times \dfrac{106}{84}$	0.21	
Total		51.69

From the foregoing results it is proved beyond doubt that the bicarbonate actually contains normal sodium carbonate (Na_2CO_3) which is present to the extent of $7 \pm$ per cent. When the acidic and basic constituents from the analysis are combined to form various salts, it is found that there is a surplus of Na^+ unaccounted for and at the same time also a corresponding surplus of CO_3^{--}. after all possible acidic radicals have been combined with Na^+ and the small amounts of NH_4^+ and Mg^{++} present. Independent checks from the "yields" of the bicarbonate and from the losses on ignition both give concordant results. So it can be concluded that the normal carbonate is present in the sample of the crude bicarbonate from the filters. Study of the mother liquor from the towers shows that this sodium carbonate is largely formed by the rapid loss of carbon dioxide on exposure to the air (see Chapter XI). Further, if the fresh solution of the crude bicarbonate is immediately taken from the filter without exposure to the air, it gives no coloration to phenolphthalein at first. However, the red color develops gradually but increases rapidly on standing *i.e.*, on exposure to the air.

Some ammonium bicarbonate is also found to be present to the extent of about 5 per cent NH_4HCO_3 on the weight of dry $NaHCO_3$ in the crude bicarbonate from the filters. The presence of NH_4HCO_3 is due to an entirely different source, however. No matter how thoroughly the crude bicarbonate on the filter has been washed, some NH_4HCO_3 is always found —in fact in a definite percentage of ammonium bicarbonate on the weight of dry sodium bicarbonate obtained. It would thus be seen that NH_4HCO_3 and $NaHCO_3$ have separated in the columns in the form of a solid solution with a definite ratio between them. This molar ratio is 1 mol NH_4HCO_3 per 19 mols $NaHCO_3$, which gives approximately 5.0 per cent NH_4HCO_3.

The size of the crystals of the bicarbonate formed in the towers has an important bearing on the drying properties of the bicarbonate in the dryers. When the bicarbonate crystals are coarser, they filter better, wash better, and come drier, *i.e.*, the moisture content is lower and the "yield" in Na_2CO_3 higher. Drier bicarbonate always means less tendency to scale formation in the dryer, less returned ash required, larger drying capacity for the dryer, and less coal consumption in the furnace per ton of soda ash calcined. When the bicarbonate crystals are coarser, a thicker layer of bicarbonate (as much as $\frac{5}{8}$ inch thick) can be picked up on the filter, even though a smaller vacuum is required. Poor crystals, formed from cold towers, for instance, require a high vacuum for filtering (as much as 12 to 18 inches Hg); yet only a thin layer can be picked up, yielding a wet bicarbonate which is difficult to dry and which contains high sodium chloride. This cuts down the capacity of the filter as well as that of the dryer. Bicarbonate that will not produce any slimy juice on long squeezing and forced kneading in the palm of the hand will dry without difficulty. This is a rough and ready test for the quality of the bicarbonate. Bicarbonate having a "yield" of more than 47.5 per cent will not produce any slimy juice in this way, nor stick together to form

a ball in the hand. Good bicarbonate crystals should feel granular, like fine sand between fingers, while poor crystals will feel sticky, like a starch paste. Good, coarse crystals will settle to a compact sludge in a 100-cc. cylinder in less than three minutes, while poor ones will require a much longer time (7 to 10 minutes), and they will not settle to a compact sludge but to a voluminous, mobile, slimy paste. Too high a draw temperature may also produce this condition because of partial re-solution of the bicarbonate crystals in the liquor. Under normal conditions, the volume of the completely settled bicarbonate at the bottom of the glass cylinder should be 40 to 45 per cent of the total volume of the tower draw sample. But when the crystals are poor, the precipitate is less compact and may occupy a volume of 50-55 per cent. The percentage of suspended solids (NaHCO$_3$ crystals, etc.) in the slurry from the columns generally runs 20.5-21.0 per cent by weight.

As mentioned above, filtration of crude bicarbonate by means of continuous, rotary vacuum filters has been most generally employed in ammonia soda plants This is essentially a constant-pressure filtration, in which the pressure differential between the atmospheric pressure outside the drum and the partial vacuum inside furnishes the driving force. In ammonia soda plants, the rate of draw from the columns to the filters is maintained constant, and so is the output from each filter. Due to the care exercised to maintain the crystal size, the thickness of the cake on the filter and the vacuum required are practically constant day in and day out. To understand better the principles underlying filtration, we may pause for a few moments to dwell briefly on some theoretical discussion. Not unlike a filter press, the cake on the filter has to be built up under a pressure differential to a desired thickness from solids caught on the surface of the filtering medium when the liquid is forced through. It is thus seen that the resistance through the cake increases proportionally as the thickness of the cake that is being built up, other conditions being equal, and so also increases proportionally as the volume of the filtrate that is being collected At the same time it is also easily seen that this resistance varies inversely as the filter area. The filtering medium in the form of a woolen felt possesses numerous pores through which liquor passes, closely approximating the condition of flow called for in Poiseuille's law, i e., the pressure drop across the filtering medium is directly proportional to the viscosity of the liquid, the velocity of the flow, and the length of the path; and it is inversely proportional to the cross-sectional area From the slowness of infiltration of the liquor through the pores of the cake and of the blanket, it is safe to assume that the flow within these pores would be "viscous" or "streamline," and we may expect Poiseuille's law to hold. Under these conditions, we may expect the rate of filtration to be:

$$\frac{dV}{d\theta} \propto \frac{AP}{\mu R}$$

where V = volume of the filtrate in cu. ft. passing through the filter;
θ = time of filtration in sec.;
A = area of filter in sq. ft.;
P = pressure differential in lb. per sq. ft.;
μ = viscosity of the liquor in poises;
R = characteristic constant depending on resistance of the cake, etc.

For a given filter operating on a given liquor at a substantially constant-pressure differential, $\dfrac{AP}{\mu}$ is a constant ($= K'$), *i.e.*,

$$\frac{dV}{d\theta} = \frac{K'}{R}$$

But, as mentioned above, the resistance of the cake depends upon the thickness of the cake being built up, which in turn varies as the volume of the filtrate passing through the filtering medium.

Therefore $\dfrac{dV}{d\theta} = \dfrac{K}{V}$, where K is now a combined constant
or $V\,dV = K\,d\theta$

Integrating we get

$$(V + V_c)^2 = K(\theta + \theta_o),$$

where V_c is an integration constant having the significance of an initial volume of filtrate building up an imaginary thickness of a cake having the same resistance as the filtering medium iteslf, and θ_r a constant establishing the starting time from which this imaginary cake may be said to have been formed.* The curve showing the relationship between the volume of the filtrate passing through (V) and the time of building up the cake (θ) is thus a parabola, and is true of a constant-pressure filtration operation, such as in the filtration of the crude bicarbonate from the columns, where the solids are highly crystalline and the cake is substantially non-compressible under the pressure differential employed.

As mentioned above, a centrifugal filter is sometimes used as a final filter, which brings the moisture content in the bicarbonate down still further to about 58 per cent of the yield, with the moisture content less than 7 per cent. Sometimes the moisture content in the bicarbonate from the centrifuge is claimed to be as low as 4 per cent, *i.e.*, the yield as high as 60 per cent. Under such conditions little returned ash would be required in drying the bicarbonate in the rotary dryers. The centrifugal filter is, however, an intermittent machine operating in batches with a bottom discharge for the vertical type, and side discharge for the horizontal type. It revolves at from 1000 to 1800 r.p.m. A batch-type machine with a 48-inch basket will produce 30-35 tons of bicarbonate per 24 hours. The intermittency of the batch and the difficulty of keeping down the loss of ammonia caused a serious problem in the adaptation of the

* Ruth, B. F., Studies in Filtration. III. Derivation of General Filtration Equations, *Ind. Eng. Chem.*, **27**, 708 (1935); Studies in Filtration, IV. Nature of Flow through Filter Septa and Its Importance·in the Filtration Equation, *Ibid.*, **27**, 806 (1935).

centrifugal to soda-ash manufacture. However, the use of centrifugals for filtering is more general in connection with the manufacture of refined sodium bicarbonate (see Chapter XVIII). A continuous centrifuge is now offered in the market. It greatly cuts down the labor of handling and increases the output per unit with a saving in floor space.

Continuous centrifuges may be classified into two types. One is the automatic type which is continuous as regards the different operations in the cycle, but intermittent in feeding and unloading. It is really an automatic intermittent machine. The other type is a strictly continuous one, both taking the feed and discharging the cake continuously. To avoid confusion we shall refer to the former as the "automatic" type and the

Fig. 39. Continuous centrifuge (screen type).

latter as the "continuous" type. The automatic machines are generally horizontal and have a speed of from 500 r.p.m. in the large machines to 1800 r.p.m. in the small ones (with a basket of small diameter). They may be single or double (*i.e.*, single basket, or double baskets placed back to back).

The continuous type, *i.e.*, one having the slurry fed continuously at one end of the basket and the dried crystals unloaded at the other end, is, generally speaking, still in the process of development as far as the filtration of crude bicarbonate (ammonia soda) is concerned, and has so far been confronted with several mechanical difficulties. Some of these may be mentioned here. For very fine crystals (such as $NaHCO_3$), this continuous type requires a very large number of extremely fine slits in the basket (such as 0.004 to 0.006 inch wide by $\frac{3}{4}$ to 1 inch long) which is

rather difficult and expensive to make The screen is either cut from a solid plate or made up of a large number of special-shaped bars of uniform cross-section Even then, the smaller crystals (the fines) are apt to pass through the screen and find their way to the filtrate This is sometimes a very serious matter if the filtrate is to be processed subsequently Furthermore, the mechanism of transferring (or conveying, or pushing) the crystals on the screen from the feed end to the discharge end, is generally a difficult problem because of the high speed This mechanism is now either in the shape of a ribbon screw conveyor, running at a differential speed to the basket, usually at a differential of from 1/60 to 1/80 of the basket speed, as in the Bird continuous machine *

Courtesy Escher Wyss Engineering Works Ltd

FIG 40   Continuous centrifuge (pusher type)

(Fig 39), or in the form of a piston pusher making 8 to 18 strokes per minute with the length of stroke about 40 mm, as in the Escher Wyss continuous machine † (Fig 40)   The push-type mechanism runs very smoothly and has no tendency to crush the crystals in the basket The differential speed conveyor as developed by the Bird Machine Co is now operating steadily and stably, but the ribbon conveyor edge has a scraping action, grinding the crystals forward over the surface layer of the cake in the basket Both types at the present stage require the crystal size to be no finer than 0 20 mm, or 65 mesh, and are not adaptable to crystals finer than 0 10 mm, or 150 mesh, otherwise too much of the fines would
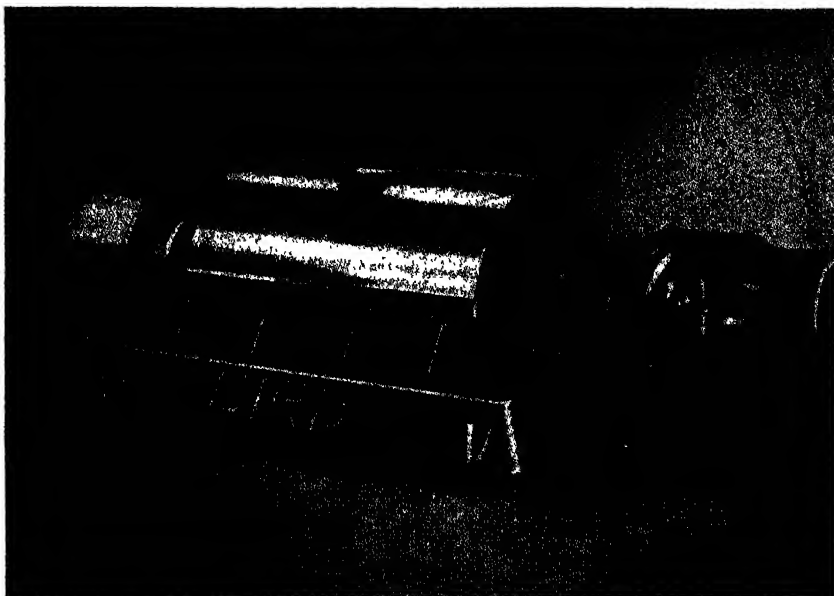
(a) *Casing on.*
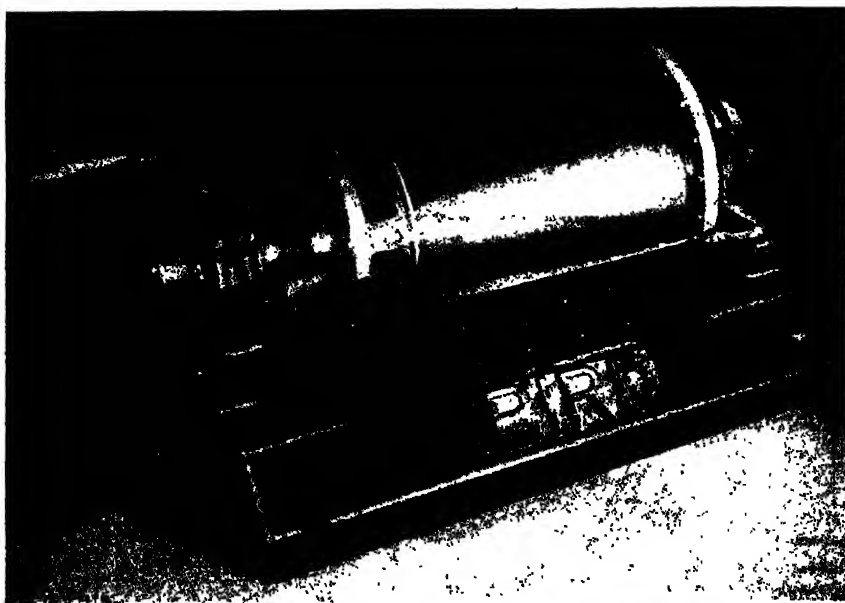
(b) *Casing removed.*

FIG. 41. Bird solid bowl centrifugal filter.

pass through the screen. To meet this difficulty, the Bird Machine Co. put out a solid bowl machine having solid walls in the "basket" (*i.e.*, doing away with the slots and depending solely upon the centrifugal action to separate the solids from the liquid in the bowl (Fig. 41). The machine is otherwise no different from the continuous basket type. This solid bowl machine is particularly suitable for handling fine slimes, such as cement, clay, sewage sludge, lithopone pigment, etc. But for bicarbonate of soda crystals, it is not so satisfactory, because it has a tendency to break up
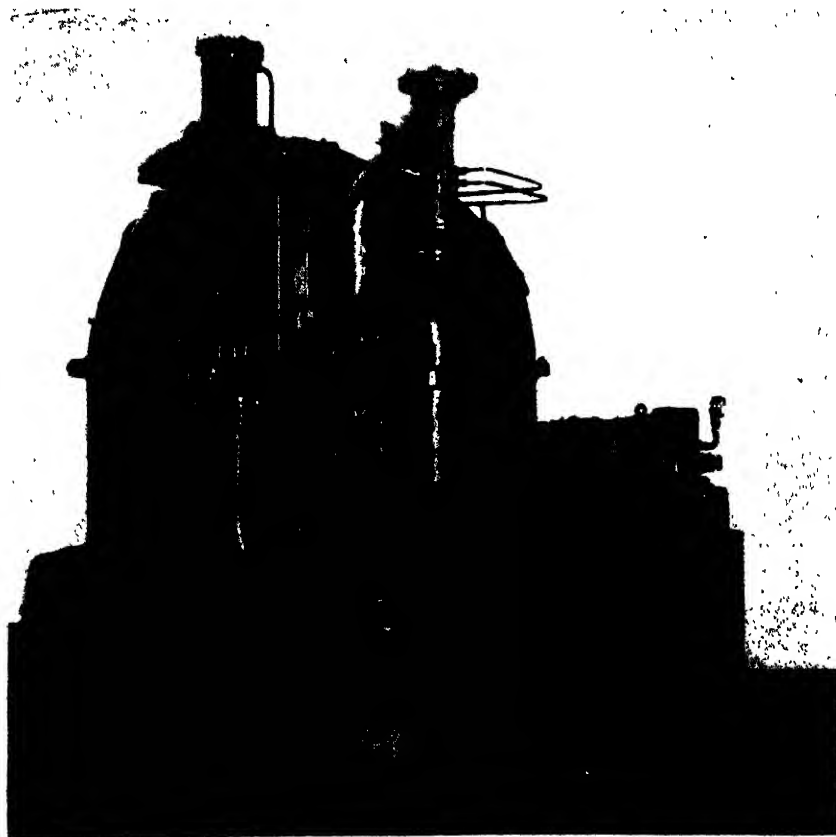
Courtesy Escher Wyss Engineering Works, Ltd.

FIG. 42. Escher Wyss (ter Meer) automatic centrifuge.

the crystals and knead them into a dough-like mass, so that the dryness or "yield" of the bicarbonate obtained is not much better than the "yield" obtainable from a well-designed modern rotary vacuum filter. Strange to say, however, bicarbonate of soda crystals could be handled in the ordinary batch-type, vertical, suspended centrifuges, without such difficulties, and these centrifuges are used extensively for refined bicarbonate of soda, as mentioned above.

At present, only certain of the automatic type centrifuges—notably the Escher Wyss (ter Meer) automatic machine (Fig. 42)—have been used for the crude bicarbonate of soda service in place of rotary filters. This ter Meer automatic will handle the fine crystals of bicarbonate of soda because of the special feature in its basket construction, but more particularly because it also uses a woolen felt as the filtering medium (Fig. 43). The dryness obtained is 8-10 per cent moisture, depending upon the size of the bicarbonate of soda crystals from the columns.
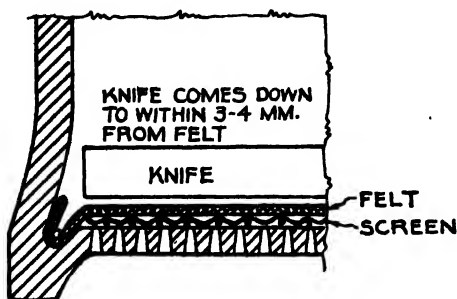
Fig. 43.

Escher Wyss automatic centrifuge using felt as filtering medium.

On the other hand, these automatic centrifuges are very well suited to the drying of coarse crystals, *e.g.*, NaCl, NH$_4$Cl, (NH$_4$)$_2$SO$_4$, Na$_2$SO$_4$, CuSO$_4$, or other substances that habitually crystallize in large crystals. The better known ones are the ter Meer automatic of from 1700 to 2100 mm. diameter, and the Sharples 63″ automatic and 20″ Super-D-Hydrator.[*]

As regards the cycle or the period of intermittency, these automatic machines vary widely. For example, the Sharples Super-D-Hydrator with 20″ basket has a cycle of only 45 seconds, while a large ter Meer machine has a cycle of 18-20 minutes. Other automatic machines such as the Haubold machine [†] have a cycle of from 4 to 7 minutes. These cycles

TABLE 75. Timing of Events in a Cycle of Automatic Centrifuge.

Events	Sharples Super-D-Hydrator	Sharples 63″ Automatic	Escher Wyss "ter Meer" Automatic 1700 mm.	Escher Wyss "ter Meer" Single Automatic 2100 mm.
Feeding	8 sec.	1 min.	4 min.	5 min.
First drying	4 "	½ "	1 "	1 "
Rinsing	6 "	¼ "	4 "	3 "
Drying (spinning)	21 "	2½ "	7 "	8 "
Unloading	6 "	½ "	2 "	3 "
Total	45 sec.	4½ min.	18 min.	20 min.
Vol. in basket	1 cu. ft.	7.8 cu. ft.	0.56 M³	1.05 M³
Speed	1800 r.p.m.	480 r.p.m.	700 r.p.m.	550 r.p.m.
Horsepower	20 H.P.	30 H.P.	30 KW	45 KW
Centrifugal force	920 × gravity	206 × gravity	440 × gravity	338 × gravity

[*] The Sharples Specialty Company, Philadelphia, Pa.
[†] Haubold Maschinenfabrik, Chemnitz, Germany.

are, however, adjustable within a certain range. Table 75 illustrates the distribution of time among the several events in the cycle in some typical makes.

The present tendency is to go to smaller diameters, but higher speeds (Sharples Super-D-Hydrator, 20″ diameter, and the Bird continuous, 18″ diameter) with smaller amounts of material in the baskets. According to the simple laws of physics,

If α = acceleration in feet per sec. per sec.
  v = peripheral velocity in feet per sec.
  r = radius of basket in feet

Then $\alpha = \dfrac{v^2}{r}$

Let W = weight of crystals in the basket in lbs.
  $\dfrac{W}{g}$ = mass of crystals in the basket = m
  F = centrifugal force developed in lbs.
  N = r.p.m. of the basket
  ω = its angular velocity = $\dfrac{2\pi N}{60} = \dfrac{v}{r}$ radians

Therefore $F = m\alpha = \dfrac{W}{g} \cdot \dfrac{v^2}{r} = \dfrac{W}{g}\,\omega^2 r$ lbs.

  $= \dfrac{W}{32.2} \cdot \left(\dfrac{2\pi N}{60}\right)^2 \cdot r$ lbs.

Therefore $F = 0.000341\, W\, N^2 r$ lbs.

One often speaks of the centrifugal force developed as being so many times gravity. This means so many times the weight of its mass. Thus,

$$\frac{F}{W} = 0.000341\, N^2 r \text{ (times gravity)}$$

This centrifugal force as developed commercially varies within a wide range of from 200 to 1800 times gravity, the higher figure being for speeds as high as 1800 r.p.m., using a 40-inch basket in a batch type machine. Normally, a high-speed commercial centrifuge develops about a thousand times gravity.

It is apparent that the greater the centrifugal force, the greater the drying power, or for the same dryness, the shorter the time required for spinning. Now, to accomplish this, either the speed, N, or the radius of the basket, r, must be increased. But since the centrifugal force is increased as the square of the speed, but only linearly as the diameter, it is advantageous to increase the speed rather than the diameter. Also, from the consideration of mechanical strength, it is also desirable to keep the diameter small. Hence the tendency of the design for a good factor of safety is rather to have a smaller basket with a correspondingly smaller mass in it, working at a higher speed, than to have a larger diameter, larger volume and consequently greater mass.

The following screen analyses on some of the typical crystals, such as $NaCl$, $(NH_4)_2SO_4$, NH_4Cl, NH_4HCO_3 and $NaHCO_3$, are given to illus-

TABLE 76. Screen Analyses of Some Typical Crystals.

Crystals Mesh	Opening mm	Evaporator Salt (NaCl) Retained on %	Cumulative %	By-Product Ammonium Sulphate [(NH4)2SO4] Retained on %	Cumulative %	Crude Ammonium Chloride (NH4Cl) Retained on %	Cumulative %	Refined Ammonium Chloride (NH4Cl) Retained on %	Cumulative %	Ammonium Bicarbonate (NH4HCO3) Retained on %	Cumulative %	Crude Sodium Bicarbonate (NaHCO3) (Ammonia Soda) Retained on %	Cumulative %	Refined Sodium Bicarbonate (NaHCO3) Retained on %	Cumulative %
20	0.833	0.000	0.000	0.000	0.000	0.000	0.000	1.180	1.180	0.280	0.280	0.000	0.000	0.000	0.000
28	0.589	0.000	0.000	3.107	3.107	5.116	5.116	3.650	4.830	2.040	2.320	0.000	0.000	0.000	0.000
35	0.417	5.893	5.892	29.405	32.512	25.680	30.796	18.784	23.614	3.320	5.640	0.050	0.050	0.149	0.149
48	0.295	54.869	60.761	37.834	70.343	38.334	69.120	33.564	57.178	8.880	14.520	1.502	1.552	0.826	0.975
65	0.208	32.541	93.302	21.580	91.926	16.426	85.556	27.180	84.358	15.450	29.970	4.896	6.448	3.523	4.498
100	0.147	6.264	99.566	5.762	97.688	10.354	95.910	12.730	97.088	19.180	49.120	14.369	20.817	7.126	11.624
150	0.104	0.434	100.000	1.819	99.507	3.344	99.254	2.452	99.540	16.380	65.500	25.883	46.700	17.765	29.389
Through 150	0.104	0.000		0.493		0.746		0.450		34.500		53.305		70.611	

trate the range of crystal size ordinarily met with in industrial plants (see Table 76). It can be seen that the refined bicarbonate of soda has the smallest crystals among them; next comes the crude bicarbonate of soda (ammonia soda). Crystals such as NaCl, $(NH_4)_2SO_4$, NH_4Cl and the like, which have over 80 per cent larger than 0.20 mm. or coarser than (retained on) 65 mesh, are all suitable for use in the continuous centrifuges developed at the present time. Crystals such as refined $NaHCO_3$, over 50 per cent of which will pass through 150 mesh, cannot be used on the continuous machine, using metal screens. The Bird Machine Company's solid bowl machine, which has no screen at all, is unique among all types of continuous machines in that it can handle any fine, slimy solids down to even the cement size. This solid bowl machine will handle sodium bicarbonate crystals (crude or refined), but the moisture content in the cake is not less than that obtainable from a high-yield rotary vacuum filter. Further, the bicarbonate cake obtained from the solid bowl machine becomes denser and glazed because of the kneading action of the screw conveyor on the crystals.

From the above, it can be safely said, as regards continuous type centrifuges in general, that they have so far not found satisfactory application in the ammonia-soda service. But because of their strictly continuous character and because of the higher "yield" possible, there always exists a temptation to try to adapt them to the ammonia-soda industry; indeed extensive efforts are being made in this direction. There are, however, certain drawbacks to their use, among which are (1) that the cost of the machine is far too great as compared to the capacity obtainable, and (2) that the power required to drive such a machine is also greater. Compare this with a moderate sized, continuous, rotary, vacuum filter of the latest high-yield type, which has a capacity of 200-300 tons of soda ash per day (*i.e.*, 300-500 tons in terms of sodium bicarbonate per day), requiring only a 5 H.P. motor to drive it, taking into consideration the fact that the difference in the "yield" obtained from the filter vs. the continuous centrifugal may be only a trifle.

Also, with the advent of the continuous and automatic horizontal machines, it does not necessarily follow that the batch-type, vertical, suspended centrifuges will be entirely superseded. Nowadays, these batch-type centrifuges (which, since they are most generally used in the sugar industry, have become known as "sugar centrifugals") have also been brought to a high degree of perfection. A 48-inch vertical-suspended machine is now capable of operating at 1200 r.p.m., while a 40-inch machine may now run at as high as 1800 r.p.m. Being suspended and free to seek its balance, this batch-type vertical machine may be operated safely at a higher speed than a two-bearing or overhung horizontal continuous machine of the same basket diameter. Further, certain automatic mechanisms, such as the charging and unloading devices, may now also be fitted to these batch-type machines, so that one person also can look after a number of them at the same time. .

As regards the crystalline forms of the four main salts in equilib-

rium in the liquor, the crystals of sodium chloride are of course cubic (isometric); those of sodium bicarbonate monoclinic; those of ammonium bicarbonate are also monoclinic; and those of ammonium chloride isometric or tetragonal. Under normal operating conditions, the ammoniated brine is undersaturated with respect to sodium chloride, and so no crystals of sodium chloride should deposit out. Because of the mode of formation in the towers, the crystals of sodium bicarbonate are necessarily small. Under a microscope even at a magnification of 400 diameters, these bicarbonate crystals appear merely as long rods, the individual shape of the rod being still difficult to examine. This is because of the violent stirring effect due to the bubbling of the carbon dioxide gases in the tower, with the result that the crystals formed are very small, especially when the tower temperature has not been properly regulated or when the carbon dioxide gas delivered to the tower is greatly weakened. These bicarbonate crystals have a "twinning" habit and often form "daisies." These are seldom seen as perfect, well-developed, crystal individuals. As seen under a microscope, a few of these crystals are very large, but these are rather agglomerations of many individuals. Under good operating conditions, the size of the average crystals as seen under a microscope and estimated on a "counting chamber" is between 100 and 200 microns (00.10-0.20 mm), while under poor operating conditions yielding a pasty sludge, the size may be between 50 and 100 microns (0.05-0.10 mm.) or smaller.

Under certain conditions the crystals of ammonium bicarbonate may be deposited with the sodium bicarbonate. If this happens, it will be seen that they are coarser and are more plate-like in formation, quite different from the rod formation of the sodium bicarbonate, though belonging to the same system (monoclinic). The crystals of ammonium chloride are not formed under these conditions because it is extremely soluble and exists in the solution far below saturation point. Consequently, there are only the crystals of sodium bicarbonate and, to a much smaller extent, of ammonium bicarbonate, to be considered in this reaction, since the other salts, sodium and ammonium chlorides, are merely carried by the mother liquor which has not been completely washed from the crystal cake.

Good tower control should include a daily photomicrographic study of the bicarbonate crystals from the towers. Not only must these crystals be maintained coarse and filterable but they should be of uniform size, free as far as possible from the secondary smaller crystals.

Attempts have also been made to study the composition of the mother liquor from the towers. It is of a much more complex character than the precipitated sodium bicarbonate with which it is in equilibrium. The result of this investigation will be given in the following chapter.

Chapter XI

Composition of Mother Liquor from Carbonating Towers

Chemical reactions taking place in the carbonating towers are of a most complex character. They are so-called ionic reactions with the soluble components in reversible equilibria with the solid phase in the form of the precipitated sodium bicarbonate and possibly also ammonium bicarbonate. These equilibrium points shift with the change of temperature so that the draw liquor from the carbonating towers must be studied at the temperature of the draw, and kept at this temperature. Not only does the solubility of the sodium bicarbonate formed increase with the rise of the temperature in the draw, but the main reaction

$$NaCl + NH_4HCO_3 \rightleftharpoons NaHCO_3 + NH_4Cl$$
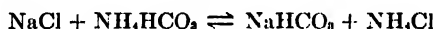
is reversed by the rise in temperature (i.e., from the solid bicarbonate formed in contact with ammonium chloride in solution, sodium chloride can be re-formed with the rise of temperature). Equilibria among the various salts in the solution phase, i.e., in the mother liquor, also change with the temperature. There are eight different kinds of ions in solution (NH_4^+, H^+, OH^-, Cl^-, HCO_3^-, $CO_3^=$, Na^+, SO_4) not including the small amount of sulfide present; and from these, at least nine different conventional combinations can exist. It is a difficult matter to determine the exact amount of each of these constituents present in solution. Any heating to which the solution is subjected in the course of chemical analysis tends to alter the equilibrium conditions; and where this is necessary, only

$$2NaCl + 2NH_4HCO_3 \rightleftharpoons 2NaHCO_3 + 2NH_4Cl$$

2NH₄ + H₂O   CO₂ + H₂O

2NH₄OH + H₂CO₃ ⇌ (H₄)₂CO₃ + H₂CO₃   H₂CO₃ + Na₂CO₃   (₂)₂CO₃ ⇌ Na₂CO₃ + 2NaCl +
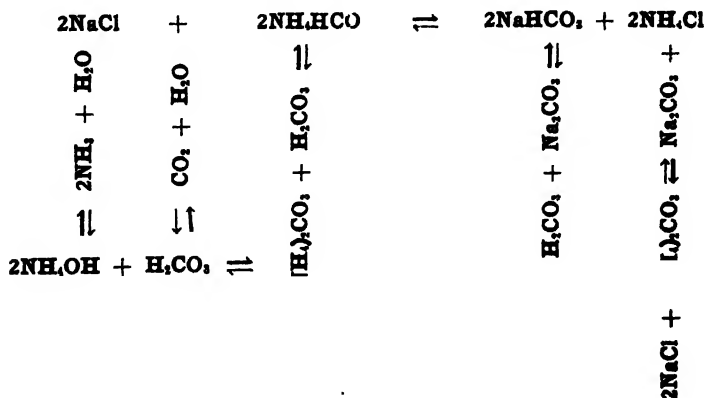
the total quantities of the components in question (regardless of whatever combinations they enter into) can be determined. Hence most of the analytical results can be expressed only as *total* quantities present. It has been found insufficient, however, to determine the quantities of all the individual components from these total-quantity determinations without the help of the physicochemical relationship, as will be seen in the following discussion.

To illustrate the complexities of these salts in the mother liquor, the above physicochemical equilibria are given on page 185. The heavier arrow indicates the predominating tendency for the components to exist in the combinations shown on one side of the equilibrium equation.

Before we proceed to give the methods of determination and the calculations necessary to obtain the desired results, we shall first give the analyses and data covering the ammoniated brine fed to the towers and also the tower-operating conditions at this particular period.

For convenience in calculation and comparison, the analytical results are expressed in the number of cc. of normal solutions per 10 cc. of the draw liquor. These then are converted into the number of equivalents per liter by simply shifting the decimal point one place to the left. Finally the concentration of each constituent thus found is given in grams per liter.

Data concerning ammoniated brine:

(1) Temperature of ammoniated brine as introduced to the towers—49.3° C.
(2) Specific gravity of ammoniated brine as introduced to the towers—1.170 at 20° C.
(3) Total ammonia—50.988 cc. N solution per 10 cc. sample (or 101.976 titer)
      Free ammonia—48.396 cc. per 10 cc. sample   (or 96.792 titer)
      Fixed ammonia—2.592 cc. per 10 cc. sample   (or   5.184 titer)
(4) Total chlorine—44.570 cc. per 10 cc. sample   (or 89.140 titer)
(5) SO_3 as $(NH_4)_2SO_4$—0.634 cc. per 10 cc. sample   (or   1.268 titer)

The operating conditions of the particular column from which the draw liquor was obtained were as follows:

(1) Draw temperature .... 30.0° C.
(2) Temperature of the reaction zone about two-thirds of
    the height of the tower .... 63.0° C.
(3) Temperature of cooling water at exit from top of cool-
    ing suction ... . 29.0° C.
(4) Temperature of cooling water at exit from bleeding
    point (at the 4th ring from bottom) .... 19.0° C.
(5) CO_2 in tower exit gas .... 6.3% by volume
(6) Inlet mixed gas to towers .... 54.0% by volume
(7) Volume of bicarbonate after 5 min. settling .... 44.0% by volume
(8) Sp. gr. of draw liquor (clear portion) .... 1.126 at 20.5° C.

We shall give in some detail the analytical methods employed and the calculations made to obtain the desired results.

(1) *SO_3 as $(NH_4)_2SO_4$.* This is determined in the usual way by acidifying with HCl and precipitating with $BaCl_2$ in hot solution. As practically all sulfates come from gypsum ($CaSO_4$) in the case of rock salt or from $MgSO_4$ and $CaSO_4$ in the case of sea salt, they are con-

verted to $(NH_4)_2SO_4$ by ammoniation when $CaCO_3$, and $MgCO_3$ or $(NH_4)_2CO_3 . MgCO_3 . 4H_2O$ separate out in the form of the "mud."

$$MgSO_4 + (NH_4)_2CO_3 \rightarrow (NH_4)_2SO_4 + MgCO_3$$
$$CaSO_4 + (NH_4)_2CO_3 \rightarrow (NH_4)_2SO_4 + CaCO_3$$
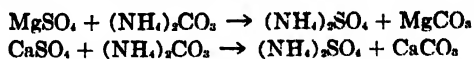
Ten cc. of the mother liquor contain $(NH_4)_2SO_4 = 0.685$ cc. N solution.

(2) *Total ammonia $(NH_4^+ + NH_3)$.* This is determined by distillation with an excess of NaOH in the usual manner. For this purpose a 5 cc. sample of the mother liquor is taken.

Ten cc. of the mother liquor contain total ammonia = 45.402 cc. N H_2SO_4.

(3) *Total alkalinity.* This is determined by taking 10 cc. of the mother liquor, adding an excess of a known amount of $N/2$ H_2SO_4 and titrating back with $N/2$ NaOH, using methyl orange as the indicator.

Ten cc. of the mother liquor = 9.440 cc. N H_2SO_4.

(4) *Total chlorides, Cl^-.* This is determined by taking an aliquot portion containing 0.500 cc. of the mother liquor, neutralizing, adding 0.2 gram $CaCO_3$, diluting it to about 100 cc., and titrating with $N/10$ $AgNO_3$, using 3 drops of 15% K_2CrO_4 as indicator. The end point is where the faintest red in the background of white AgCl precipitate is just observable.

Ten cc. of the mother liquor contain $Cl^- = 49.144$ cc. N $AgNO_3$.

(5) *Total sodium, Na^+.* Acidify an aliquot portion containing 4 cc. of the mother liquor with dilute HCl, using a small excess. Heat to boiling and remove the sulfate with a slight excess of $BaCl_2$. Filter and wash with hot water. Make the filtrate distinctly alkaline with NH_4OH, and add a small excess of $(NH_4)_2CO_3$ and $(NH_4)_2C_2O_4$. Allow to settle, and filter by decantation and wash. Evaporate the filtrate over a gentle flame in a large casserole, and ignite gently until no fumes are seen. Dissolve the residue with a little water and transfer the solution to a small tared evaporating dish, cautiously heat to dryness and ignite over a low flame once more. Cool and weigh the NaCl residue. For an alternative method using uranyl magnesium acetates, see Chapter XXVIII, "Chemical Analyses and Tests in Alkali Industry."

Ten cc. of the mother liquor contain sodium = 13.908 cc. N solution (by calculating from the weight of NaCl).

(6) *Total CO_2.* The most accurate method for determining CO_2 is by evolution and absorption of CO_2 in a purifying and absorption train gravimetrically, as described on p. 472, Chapter XXVIII. Unfortunately the evolution and absorption method is somewhat long and tedious. The method of adding an excess of NaOH, heating, precipitating CO_2 as $BaCO_3$ by $BaCl_2$, filtering, washing and titrating the precipitated $BaCO_3$ with an acid is likely to give too high results, as it is very difficult to wash out the excess of NaOH completely from the fine precipitate of $BaCO_3$. The result may be 4 to 5 per cent too high. The method of liberating the CO_2 from solution and measuring its volume before and after absorption,

on the other hand, gives too low results. The error is due partly to the solubility of CO_2 gas in water and partly to the inaccurate theoretical factor used for reduction to standard conditions and for conversion to the weight from the volume so obtained. The figures may be a half per cent too low. The method of driving off CO_2 gas and weighing the loss in weight by means of an alkalimeter is likely to give high results because of the loss of a small amount of water vapor being counted as CO_2 gas, even if air bubbling (instead of heating) is employed to drive out all the CO_2. The result is, however, only one-half of one per cent too high, when air bubbling (without heating) is employed to drive off the CO_2. These results may not be of value for checking purposes inasmuch as the magnitude of error is sometimes much greater than some of the quantities sought, if such quantities are to be found by difference.

Ten cc. of the mother liquor contain $CO_2 = 14.245$ cc. N solution by calculating from the weight of CO_2 obtained by the evolution and absorption method above.

(7) *Ammonium chloride*, NH_4Cl.[*] This is determined by alcoholic extraction. It is found that $(NH_4)_2SO_4$, $(NH_4)_2CO_3$ and NH_4HCO_3 are very sparingly soluble in a 97 per cent or stronger alcohol. Ammonium hydroxide, which is soluble in the 97 per cent alcohol, along with the ammonium chloride, can be driven off by evaporating over a steam bath without any material loss of NH_4Cl. The detailed procedure is as follows:

Pipette 5 cc. of the mother liquor into 200 cc. absolute alcohol. Stir allow to settle and filter by decantation. Wash the residue with small portions of absolute alcohol, settle and filter, combining the washing and the original filtrate in the same beaker. Repeat the washing. Evaporate the alcohol filtrate over a steam bath to about one-half of the volume or until no alkalinity is detectable with litmus paper. Distill off ammonia from this alcoholic solution of NH_4Cl with a small excess of NaOH into an Erlenmeyer flask containing a known amount of H_2SO_4 as in the "Fixed Ammonia" determination. Evaporate off the excess alcohol from the distillate over a steam bath to about one-half of the volume. Cool, dilute with water and titrate the excess of H_2SO_4 with $N/10$ NaOH using methyl orange as the indicator. Loss of H_2SO_4 in the distillate represents fixed ammonia (NH_4Cl).

Ten cc. of the mother liquor contain $NH_4Cl = 36.062$ cc. N H_2SO_4.

A summary of the analytical results is given in Table 77.

TABLE 77. Summary of Analytical Results (in cc. N sol. per 10 cc)

$(NH_4)_2SO_4$	0 685	
Total ammonia	45.402	
Total alkalinity	9.440	
Total chlorine	49.144	
Total sodium	13 908	} by calculation
Total CO_2	14.245	} from weight
NH_4Cl	36.062	

[*] *Cf.* K. W. Jurisch, *Chem. Ztg*, pp 1091-1093 (1906).

From the analytical data in Table **77**, we next proceed to carry out different calculations, but it will be seen that the desired quantities cannot be completely determined without the help of some physicochemical relationship.

The mother liquor is alkaline to methyl orange, but barely turns phenolphthalein red; hence it is practically neutral to phenolphthalein. Let

x = no. of mols of NH_4OH per liter of the mother liquor from the column
y = no. of mols of HCO_3^- "   "   "   "   "   "   "   "   "
z = no. of mols of NH_4^+ "   "   "   "   "   "   "   "   "
r = no. of mols of H_2CO_3 "   "   "   "   "   "   "   "   "
s = no. of mols of OH^- "   "   "   "   "   "   "   "   "
t = no. of mols of H^+ "   "   "   "   "   "   "   "   "
u = no. of mols of CO_3^- "   "   "   "   "   "   "   "   "
c_1 = no. of equivalents (or normality) of total ammonia per liter of mother liquor = 4.5402.
c_2 = no. of equivalents (or normality) of total carbon dioxide per liter of mother liquor = 1.4245
c_3 = no. of equivalents (or normality) of total chlorine per liter of mother liquor = 4.9144
c_4 = no. of equivalents (or normality) of total sodium per liter of mother liquor = 1.3908
c_5 = no. of equivalents (or normality) of total sulfate radical SO_4^- per liter of mother liquor = 0.0685

Then from the total CO_2 we have

$$c_2 = 1.4245 = 2y + 2r + 2u \tag{1}$$

From total ammonia

$$c_1 = 4.5402 = z + x \tag{2}$$

From electrical neutrality or equivalent quantities of positive ions to negative ions,

$$c_4 + z + t = c_5 + c_3 + s + y + 2u$$

Since the solution is very closely neutral to phenolphthalein its pH value is not far from 8, *i.e.*, t is in the order of magnitude of 10^{-8} mol of H^+ per liter and s 10^{-6} mol of OH^-. Hence without error we can cancel out t and s.

$$c_4 + z = c_5 + c_3 + y + 2u \tag{3}$$

Also, the ionization constant of water at 25° C. is

$$K_w = 10^{-14} = ts \tag{4}$$

Now from the ionization equilibria of ammonia, and from the first hydrogen and the second hydrogen of the carbonic acid in the mother liquor, we have

$$K_b = \text{ionization constant of ammonia} = 1.8 \times 10^{-5} = \frac{sz}{x} \tag{5}$$

$$K_1 = \text{ionization constant of first hydrogen of carbonic acid} = 3.5 \times 10^{-7} = \frac{ty}{r} \tag{6}$$

$$K_2 = \text{ionization constant of second hydrogen of carbonic acid from } HCO_3^-$$
$$= 6.0 \times 10^{-11} = \frac{tu}{y} \tag{7}$$

We have here seven unknowns and seven equations, so that we are able, theoretically at least, to solve for these unknowns. But solution by simultaneous equations with the elimination of one variable after another becomes very complicated. Fortunately, the process can be shortened by solving them by the method of successive approximations, noticing that u is only about 0.006 time as large as y, and r about 0.03 time as large as y.

For from (7) $\dfrac{u}{y} = \dfrac{6.0 \times 10^{-11}}{t} = \dfrac{6.0 \times 10^{-11}}{10^{-8}} = 0.006$ (approx.)

and from (6) $\dfrac{r}{y} = \dfrac{t}{3.5 \times 10^{-7}} = \dfrac{10^{-8}}{3.5 \times 10^{-7}} = 0.03$ (approx.)

We can leave u and r out of consideration from (1) and (3) for the first approximation and then come back to correct them afterwards, and so on. Solving by successive approximations in this way we get after the third approximation the following values:

$$x = 0.2502 \text{ mol } NH_4OH \text{ per liter}$$
$$y = 0.6892 \text{ mol } HCO_3^- \text{ per liter}$$
$$z = 4.290 \text{ mols } NH_4^+ \text{ per liter}$$
$$r = 0.0187 \text{ mol } H_2CO_3 \text{ per liter}$$
$$s = 1.05 \times 10^{-6} \text{ mols } OH^- \text{ per liter}$$
$$t = 9.52 \times 10^{-9} \text{ mols } H^+ \text{ per liter}$$
$$u = 0.00434 \text{ mol } CO_3^= \text{ per liter}$$

Since from the independent determination above

$$NH_4Cl = 3.6062 \text{ equivalents per liter (normal)}$$

Therefore from the total chlorine,

$$NaCl = 4.9144 - 3.6062 = 1.3082 \text{ equivalents per liter (normal)}$$

and from the total sodium,

$$NaHCO_3 + Na_2CO_3 = 1.3908 - 1.3082 = 0.0826 \text{ equivalents per liter (normal)}$$

Again from the total ammonia,

$$NH_4HCO_3 \text{ and } (NH_4)_2CO_3 = c_1 - x - NH_4Cl - (NH_4)_2SO_4 =$$
$$4.5402 - 0.2502 - 3.6062 - 0.0685 = 0.6153 \text{ equivalents per liter (normal)}$$

The results are summarized in Table 78.

TABLE 78. Composition of Mother Liquor.

Constituents	No. of Equivalents per Liter (normality)	Grams per liter
NH_4OH (x)	0.2502	4.25 (as NH_3)
NaCl	1.3082	76.5
NH_4Cl	3.6062	193
$(NH_4)_2SO_4$ (c_3)	0.0685	4.52
$NH_4HCO_3 + (NH_4)_2CO_3$	0.6153	48.6 (all expressed as NH_4HCO_3)
$NaHCO_3 + Na_2CO_3$	0.0826	6.93 (all expressed as $NaHCO_3$)
H_2CO_3 (r)	$0.0187 \times 2 = 0.0374$	1.16 (as H_2CO_3)
Total CO_2 (diss.)	1.4245	31.3
Total "free ammonia"	0.8655	14.7 (as NH_3)

It will be seen that we have not used the data of total alkalinity. These can be used as an independent check on the accuracy of the results. Thus, total alkalinity from these results would be

$$NH_4OH + NH_4HCO_3 + (NH_4)_2CO_3 + NaHCO_3 + Na_2CO_3 = 0.9481.$$
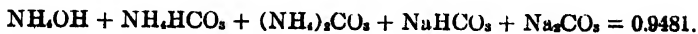
From independent titration the value obtained above is 0.9440.

From the foregoing results we can obtain important information concerning the tower operation.

In the first place, the shrinkage of volume of the ammoniated brine due to fixation of free ammonia in the towers is given by

$$(I) \quad \frac{\text{Vol. of draw liquor}}{\text{Vol. of ammoniated brine}} = \frac{4.4570}{4.9144} = 0.907 \text{ or } 9.3\% \text{ shrinkage}$$

The loss of ammonia in the form of free ammonia from the carbonating towers to the tower washer in this particular instance (and also as NH_4HCO_3 in the precipitated $NaHCO_3$) is estimated as follows:

$$(II) \quad \frac{5.0988 - 4.5402 \times 0.907}{5.0988} \times 100 = 19.2\%$$

Note that this is not representative, because the temperature of the ammoniated brine (49.3° C.) fed to the column from the cleaning tower was excessive at this particular period.

The "free ammonia titer" in the draw liquor as determined in the field by acid titration is really the sum total of

$$(III) \quad NH_4OH + NH_4HCO_3 + (NH_4)_2CO_3 + \text{diss. } NaHCO_3 + Na_2CO_3$$
$$= 0.9440 \text{ equivalents per liter. The actual value is } 0.8655 \text{ equivalents from Table 78.}$$
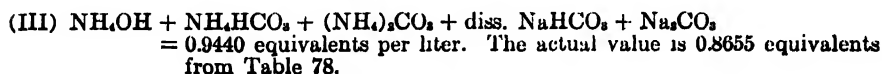
Therefore the apparent value is higher than the actual by

$$\frac{.0826}{.8655} \times 100 = 9.5\%$$

The decomposition of salt in the tower, *i.e.*, the percentage conversion or sodium chloride efficiency, is given by

(IV)

$$\frac{NH_4Cl + (NH_4)_2SO_4 - \dfrac{\text{fixed } NH_3 \text{ in ammoniated brine}}{0.907}}{NH_4Cl + (NH_4)_2SO_4 - \dfrac{\text{fixed } NH_3 \text{ in ammoniated brine}}{0.907} + NaCl \text{ (in mother liquor)}}$$

$$\times 100 = \frac{3.6062 + 0.0685 - \dfrac{0.2592}{0.907}}{3.6062 + 0.0685 - \dfrac{0.2592}{0.907} + 1.3082} \times 100 = \frac{3.3889}{4.6971} \times 100 = 72.2\%$$

The ammonia efficiency, *i.e.*, ammonia fixed in the tower from the total ammonia carried in the ammoniated brine is given by

(V)

$$NH_4Cl + (NH_4)_2SO_4 - \dfrac{\dfrac{\text{fixed } NH_3 \text{ in ammoniated brine}}{0.907}}{\text{Total ammonia in draw liquor}} \times 100 = \dfrac{3.3889}{4.5402} \times 100 = 74.6\%$$

In the mother liquor the quantity of soda dissolved is 6.93 grams of $NaHCO_3$ per liter. The percentage of soda remaining in solution from the total made in the tower is estimated as follows:

(VI)

$$\dfrac{NaHCO_3 + Na_2CO_3}{NH_4Cl + (NH_4)_2SO_4 - \dfrac{\text{fixed } NH_3 \text{ in ammoniated brine}}{0.907}} \times 100 = \dfrac{0.0826}{3.389} = 2.44\%$$

The volumes of ammoniated brine and of saturated brine required to manufacture one ton (metric and English) of 99.1 per cent (58 per cent Na_2O) soda ash are calculated as follows:

(VII)   Cubic meters ammoniated brine per metric ton of 58 per cent soda ash

$$= \dfrac{1000}{53\left[NH_4Cl + (NH_4)_2SO_4 - \dfrac{\text{fixed } NH_3 \text{ in ammoniated brine}}{0.907} - 0.0826 \right]} \times \dfrac{0.991}{0.907}$$

$$= \dfrac{1000 \times 0.991}{53 \times 3.306 \times 0.907} = 6.22$$

Cubic feet of ammoniated brine per long ton of 58 per cent soda ash = 223.

Assuming saturated brine with a saturation of 106 Cl^- titer and ammoniated brine with Cl^- titer of 89.14 as we have,

(VIII)   Cubic meters saturated brine per metric tons of 58 per cent soda ash

$$= 6.22 \times \dfrac{89.14}{106} = 5.23$$

Cubic feet of saturated brine per long ton of 58 per cent soda ash = 188.

(IX) CO_2 in the mother liquor (the somewhat diluted solution of which is known as "filtered liquor") is

$$\dfrac{14.245 \times 2 \times 22}{1000} \times \dfrac{1}{0.0019763} = 317 \text{ cc. } CO_2 \text{ at normal temperature and pressure}$$

per 20 cc. of solution.

The amount of CO_2 in the mother liquor from the towers, however, increases as the "free titer" in the green liquor and consequently in the draw liquor gets higher.

From the above it will be seen that the clear portion of the mother liquor contains only an inappreciable quantity of dissolved Na_2CO_3, the total $CO_3^=$ being only 0.00434 mol $(NH_4)_2CO_3$ and Na_2CO_3 per liter. It would thus be very doubtful if there could be much sodium carbonate in the solid phase with the precipitated sodium bicarbonate in equilibrium with the liquor in the towers. Hence we must conclude that the normal sodium carbonate (soda ash) found in the bicarbonate obtained from the

filters owes its presence largely to the spontaneous decomposition of sodium bicarbonate which occurs almost instantaneously on contact with the air.

In the foregoing calculations we have made use of the electrolytic dissociation constants. We are aware that these figures are not sufficiently accurate and that there is some disagreement in the values obtained by several workers, especially in the case of the dissociation constant for the second hydrogen of carbonic acid. Further, in using these data, we have neglected the factor of the degree of ionization (or the activity coefficient) and have assumed complete dissociation for salts and none at all for ammonium hydroxide and carbonic acid, a condition not entirely justifiable in such a complex and concentrated solution as the draw liquor from the towers. Also, it must be mentioned that in the case of the un-ionized carbonic acid the total concentration really includes carbon dioxide gas dissolved and carbonic acid undissociated, according to the equilibrium: CO_2 gas (dissolved) $+ H_2O$ (undissociated) $\rightleftarrows H^+ + HCO_3^-$.[*] However, it is believed that the results obtained above were not materially affected by these assumptions, and that they are probably correct to the third significant figure.

It must be pointed out that while sodium bicarbonate must be classified as a fairly soluble salt having a solubility of the order of a hundred grams per liter at room temperature, it is rendered very much less soluble in the presence of an excess of the reagents in solution ($NaCl$ and NH_4HCO_3), which decreases its solubility to less than a tenth of its normal value when present alone in water.

[*] See "The Theory and Use of Indicators" by E. B. R. Prideaux, New York, D. Van Nostrand Co., pages 293-306.

Chapter XII

Phase Rule in Tower Reactions: Graphical Representation of Ammonia Soda Process

The reaction between sodium chloride in the ammoniated brine and ammonium bicarbonate formed in the brine represents a system of four components. Unlike the four-component system consisting of three salts with a common ion in an aqueous solution,·such as sodium, potassium and ammonium chlorides, which can be conveniently represented by the three sides of a regular tetrahedron, placing the fourth component (water) at the vertex (Fig. 44), the system, which consists of two salts in an aqueous
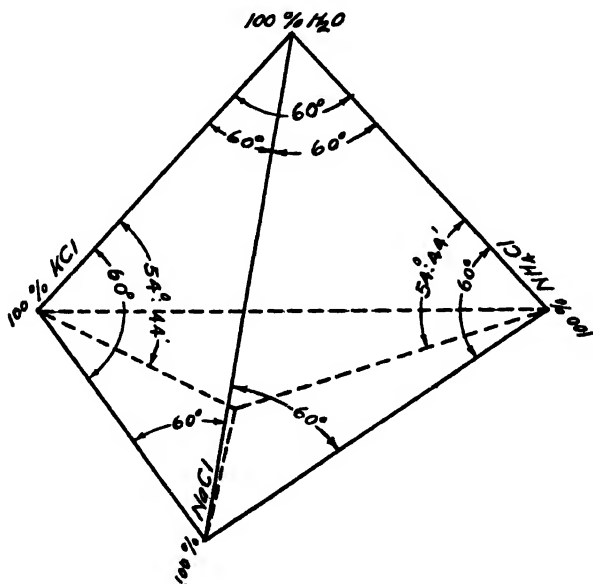
FIG. 44. For space figure.

solution with no common ions, forming together with water also a four-component system, is best represented by the four sides of one-half of a regular octahedron (Fig. 45). In this case, salts having a common ion are represented on the adjacent sides of a solid angle of the octahedron. The isothermal diagram in each case will be a plane orthogonal projection of the space figure onto the triangular base in the case of the tetrahedron (Fig. 46), or onto the square mid-section in the case of the octahedron

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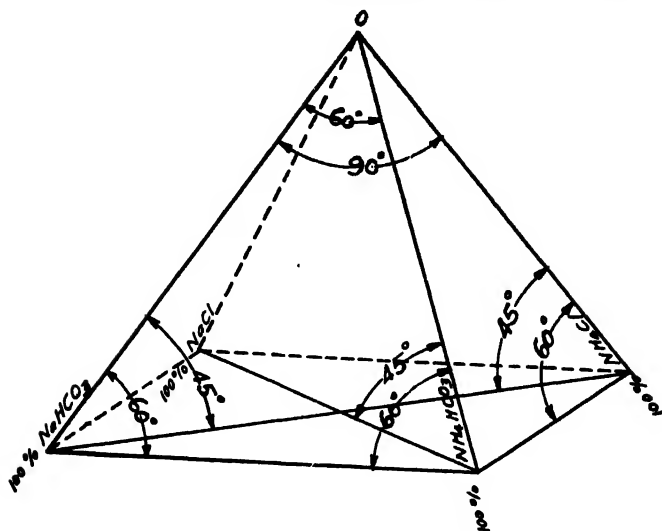
FIG. 45. For space figure (Cf. Fig. 44).

(Fig. 47). In the last case, with which we are here concerned, the isothermal diagram is represented by four rectangular coördinate axes, each axis being separate and meeting at the origin at right angles to the
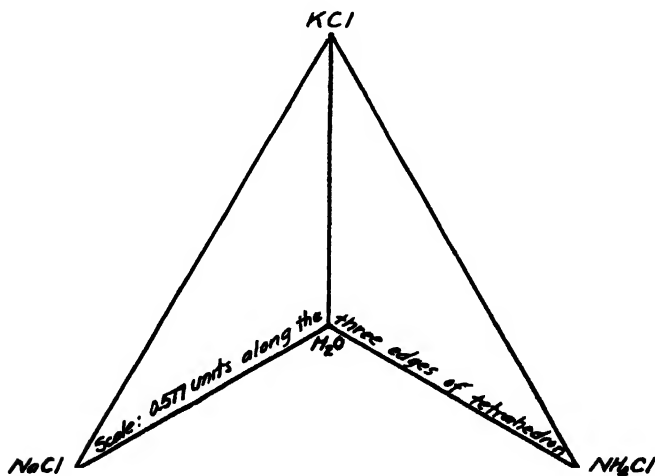
FIG. 46. For plane isothermal projection.

adjacent ones, so that they do not form two continuous axes intersecting at the origin. This isothermal diagram is nothing more or less than a plane projection from the space figure onto the square base with the units

measured along the four axes equal to $\dfrac{1}{\sqrt{2}}$ of the units measured along

the four sides of the upper half of the octahedron starting from the vertex and making an angle of 45° with the base. In this way the plane coördinate curves can be taken as representing the space figure of the octahedron at a constant temperature.

By double decomposition the two salts with no common ions can be supposed to rearrange themselves, forming another pair of salts in solution in the following fashion:

$$\overset{+-}{AB} + \overset{+-}{CD} \rightleftharpoons \overset{+-}{AD} + \overset{+-}{CB}.$$
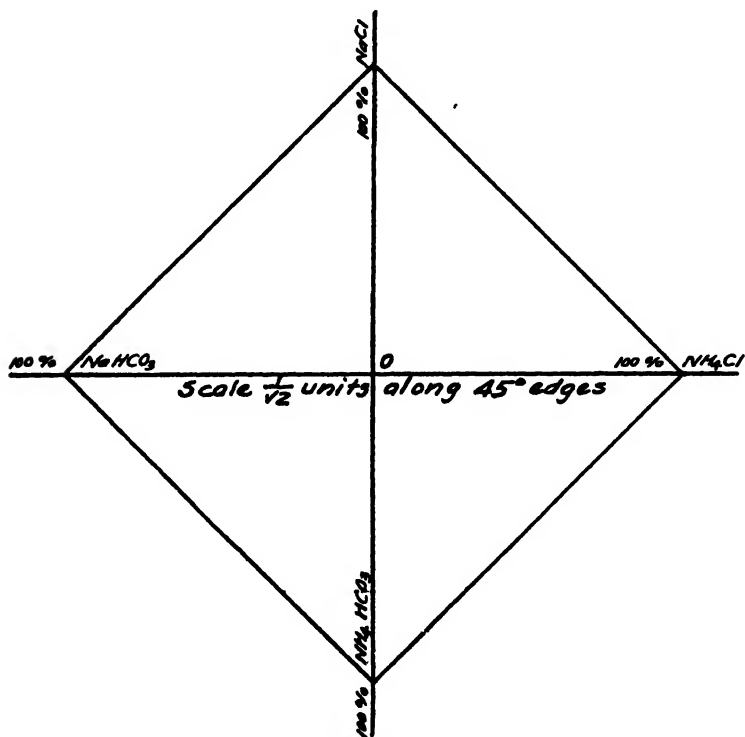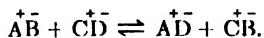
FIG. 47. For plane isothermal projection (Cf. Fig. 46)

It was from this consideration that the name "the reciprocal pairs of salts" originated. In this way there would be formed four individual salts which might be thought to constitute, together with water, a five-component system. But the four salts are so related that any three of them could determine the fourth. In other words, only three of them are independent, and the three salts, with water, form the four-component system. Thus, the tower reaction

$$NaCl + NH_4HCO_3 \rightleftharpoons NaHCO_3 + NH_4Cl$$
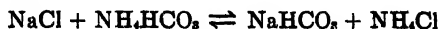
constitutes a four-component sytsem. In practice, however, an ammoniacal brine is taken and carbonated with carbon dioxide gas. Precipitation

of sodium bicarbonate progresses as the carbonation proceeds, so that ammonium bicarbonate may be said to be formed *in situ*. It is evident then that the ammoniacal brine is always saturated with carbon dioxide gas at the temperature in question. It may be thought that this carbon dioxide gas should be considered as another component, but this is taken care of by the restriction imposed that the partial pressure of carbon dioxide, together with the partial pressures of ammonia and water, must add up to a given total pressure above the solution. Since in this heterogeneous system we must have a vapor phase and a solution, the maximum possible number of solid phases at the invariant point would be four.

Degrees of Freedom + No. of Phases = No. of Components + 2 = 6.

At a given temperature we have used up one degree of freedom, and the number of solid phases possible is then only three. The number of combinations of three out of a total of four salts is $\dfrac{4 \times 3 \times 2}{3!} = 4$. These four possible cases are enumerated below:

(1) Solid $NaCl$ + solid NH_4HCO_3 + solid NH_4Cl in co-existence with solution;

(2) Solid $NaCl$ + solid NH_4HCO_3 + solid $NaHCO_3$ in co-existence with solution;

(3) Solid $NaCl$ + solid NH_4Cl + solid $NaHCO_3$ in co-existence with solution;

(4) Solid $NaHCO_3$ + solid NH_4HCO_3 + solid NH_4Cl in co-existence with solution.

Returning to the general expression above, $\overset{+-}{AB} + \overset{+-}{CD} = \overset{+-}{AD} + \overset{+-}{CB}$, when the four solid salts are in equilibrium with the solution we have the product of molal concentrations of the salts $\overset{+-}{AB}$ and $\overset{+-}{CD}$ equal to that of the molal concentrations of $\overset{+-}{AD}$ and $\overset{+-}{CB}$. This is a necessary condition for the two pairs of solid salts $\overset{+-}{AB} - \overset{+-}{CD}$ and $\overset{+-}{AD} - \overset{+-}{CB}$ to be in stable equilibrium with each other and with the solution. If the product of solubilities of one pair of the solid salts $\overset{+-}{AB}$ and $\overset{+-}{CD}$ is greater than the corresponding product of the solid salts $\overset{+-}{AD}$ and $\overset{+-}{CB}$ at the same temperature, the first pair are said to be in a metastable equilibrium with the second pair and will disappear, yielding the second pair as the solid phase in contact with the solution. Conversely, if the product of solubilities of the second pair of salts, $\overset{+-}{AD}$ and $\overset{+-}{CB}$, is greater than the corresponding product of the first pair, $\overset{+-}{AB}$ and $\overset{+-}{CD}$, the second pair will disappear, leaving the first pair in a stable equilibrium with the solution. In this reaction we have the solubility relationship at different temperatures as given in Table 79, page 198.

Thus, we see that the product of solubilities of $NaCl$ and NH_4HCO_3 at each temperature is greater than the corresponding product of $NaHCO_3$

TABLE 79.   Solubility Relationship of NaCl, NH₄HCO₃, NaHCO₃ and
NH₄Cl in Water.

Temp. (° C.)	Solubilities in Mols per Liter of Water						Ratio of Their Products
	NaCl	NH₄HCO₃	Product	NaHCO₃	NH₄Cl	Product	
0	6.09	1.51	9.20	0.82	5.50	4.52	2.03
10	6.10	2.00	12.2	0.97	6.23	6.05	2.02
15	6.11	2.32	14.2	1.07	6.58	7.07	2.01
20	6.13	2.66	16.3	1.14	6.95	7.94	2.05
25	6.14	3.03	18.6	1.23	7.36	9.06	2.05
30	6.16	3.42	21.1	1.32	7.75	10.23	2.06

and NH₄Cl, and the ratio is roughly 2 to 1 in each case. This means that at all these temperatures the coexistence of solid NaCl and solid NH₄HCO₃ in contact with the solution is in a metastable equilibrium and these two solid phases cannot exist side by side. Consequently, of the four possible combinations of the three solid salts in equilibrium with the solution enumerated above, only combinations (3) and (4) need be discussed, because both combinations (1) and (2) would involve the coexistence of solid NaCl and solid NH₄HCO₃ in contact with the solution. In the actual study at a fixed temperature there exist only two invariant points such as *J* and *K* illustrated by the isothermal diagram for 15° C. (Fig. 48).*

From the phase rule we know that each area in this plane projection represents a region where one particular salt will separate out as a solid phase from the solution of the composition given by a point within the area, and that each internal line such as *EJ*, *FJ*, *JK*, *KG*, or *KH* represents the locus where two salts represented by the two areas adjoining each other by such a line will separate out as the coexisting solid phases in contact with a solution of the composition shown by a point on this line. These are known as univariant lines. The intersections of these univariant curves give the invariant points such as *J* and *K* shown in Fig. 48. These invariant points are located by plotting the compositions of the solutions in the following manner: Set off the molal concentration of NaCl in the solution from the common point O along the NaCl-axis and the difference between the molal concentrations of NH₄Cl and NaHCO₃ from *O* along that axis which has the greater concentration. The two coördinates will determine a point. Notice that at either *J* or *K* the composition of the solution is determined by the molal concentrations of the three salts, namely NaCl, NH₄Cl and NaHCO₃, the difference between the last two being taken as one of the coördinates. But *J* and *K* represent the two invariant points at the temperature in question where three solid phases can coexist with one another and the solution. At *J*, the three solid phases are NaCl, NaHCO₃, and NH₄Cl, and at *K* they are NaHCO₃, NH₄HCO₃ and NH₄Cl. It is thus seen that at *K* the three salts separating out from the solution do not correspond exactly to those present in the solution. Hence *K* is called the "incongruent" point, while *J*, which marks the same three salts in the solid phases as in the solution

* Cf. P. P. Fedotieff, "Der Ammoniaksodaprozess vom Standpunkte der Phasenlehre," *Z. physik. Chem.*, 1904.

from which these salts separate out, is designated as the "congruent" point. It might be added here that by adding solid sodium chloride to the incongruent system, solid ammonium bicarbonate can be gradually used up until, when solid sodium chloride has been added in excess, solid sodium chloride remains in place of the solid ammonium bicarbonate and the system is again congruent.
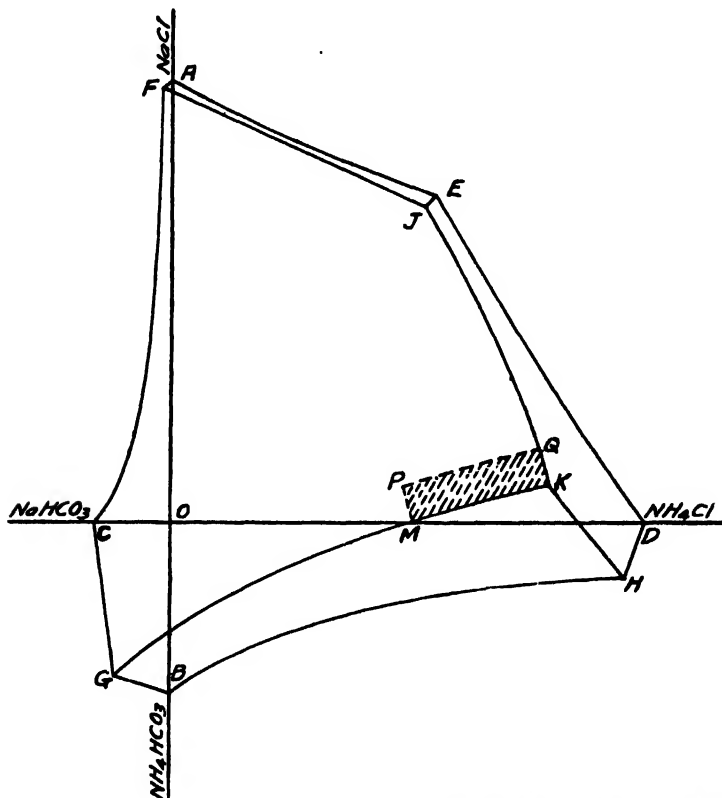
Fig. 48. Plane isothermal projection from octahedral space figure for system consisting of reciprocal pairs $NaCl + NH_4HCO_3$ and $NaHCO_3 + NH_4Cl$.

From the diagram (Fig. 48) it is seen that at 15° C. the NaCl-area does not come in contact at any point with the NH_4HCO_3-area, and as the temperature is raised the two areas do not approach each other. In other words, at all these temperatures solid sodium chloride cannot coexist with solid NH_4HCO_3 in contact with the solution. This just corroborates the above statement that the two combinations (1) and (2) are nonexistent and need not be considered.

As our aim is to precipitate sodium bicarbonate from the ammoniated brine we need only consider those three border lines of the $NaHCO_3$-area, namely GK, KJ and JF. A moment's thought will tell us that in the dia-

gram (Fig. 48) points lying higher up above O represent higher concentrations of NaCl in solution, and that points lying farther to the right of O represent greater concentrations of fixed ammonia in the form of NH_4Cl in solution. To secure a high decomposition of NaCl to $NaHCO_3$ in the towers, therefore, we must get as close to the NH_4Cl-axis from above this axis as possible, and as far to the right of O along the NH_4Cl-axis as possible. But for a high conversion of NH_4HCO_3 to NH_4Cl we must operate as far up from B and above the NH_4Cl-axis as possible. Therefore it is to be expected generally that a high percentage conversion of NaCl to $NaHCO_3$ is likely to be accompanied by a low percentage conversion of NH_4HCO_3 to NH_4Cl. As a matter of fact, percentage conversion of NH_4HCO_3 to NH_4Cl increases as we move from G to K along GK, from K to J along KJ, and from J to F along JF, until at F it reaches a maximum of 100 per cent. On the other hand, percentage conversion of NaCl to $NaHCO_3$ increases as we move down from F to J along FJ and from J to K along JK; but at K it reaches a maximum (not 100 per cent) and starts to fall off again as we move from K across the NH_4Cl-axis in the direction KG. Along FJ, NaCl can exist in the solid phase as well as $NaHCO_3$. This does not represent the actual fact, because under plant-operating conditions the NaCl concentration in the ammoniated brine employed practically never even reaches its saturation point. Therefore the curve JF need not be considered. Again, since the reaction between NaCl and NH_4HCO_3 is a reversible one, there will always be some NaCl left in the solution. That is to say, the concentration of NaCl in solution can only approach zero and is never equal to zero, and such points will lie above the NH_4Cl-axis. KG intersects the NH_4Cl-axis at M. That section of KG lying below the NH_4Cl-axis therefore has no meaning. By this elimination there are left only the curve KJ and a section KM. KJ is the curve along which NH_4Cl reaches its saturation point and tends to separate out with $NaHCO_3$ in the solid phases. Further, it is the curve along which the percentage decomposition of NaCl from the reaction decreases, the concentration of NaCl left in solution increasing as we move up from K to J. In the plant operation any possibility for solid NH_4Cl to separate out with $NaHCO_3$ is to be carefully avoided. For it would lead to a high salt content in the soda ash after calcination.

$$NH_4Cl + NaHCO_3 \rightarrow NH_3 + H_2O + CO_2 + NaCl.$$

This consideration, together with the facts that, because of mechanical perfection, the loss of ammonia in the cycle in the present-day ammonia soda plants has been reduced to a very low figure, and that the cost of ammonia is now a small item in the cost of manufacture, has dictated a condition of operation whereby a high percentage conversion of NaCl alone is aimed at. The present tendency in ammonia soda plants is to go to a higher ammonia concentration in the ammoniation operation (in the neighborhood of 100 titers of free NH_3), while making every effort to maintain as high a NaCl concentration in the ammoniated brine as pos-

sible—at best considerably below saturation with respect to NaCl. The ratio of free NH_3 to Cl^- in the resulting ammoniated brine now employed (expressed in molal concentrations) is 1.08 or even 1.12 to 1. This means that modern plants operate approximately within the narrow strip of area bordering on the short section of the curve *KM*, as shown by the shaded area in the diagram (*PQKM*), where there is a tendency for a small amount of solid NH_4HCO_3 rather than solid NH_4Cl to separate out with the precipitate of $NaHCO_3$. The presence of NH_4HCO_3 in the crude $NaHCO_3$ from the towers is less objectionable and all of it will be decomposed and recovered in the dryers.

Another revision of the conclusion reached by P. P. Fedotieff in his classical research on the ammonia soda process in 1904 is that it has not been found desirable to operate at high temperatures such as 32° C., at which point he said that both the ammonia efficiency and the sodium efficiency were 84 per cent and that there was "a greater yield of sodium bicarbonate" from the reaction. If solid ammonium bicarbonate were used in the reaction instead of the ammonium bicarbonate formed in solution by carbonating the ammonia in the brine with carbon dioxide gas, this temperature might be desirable. But as we have to bubble rather dilute carbon dioxide gases through ammoniated brine in the towers, and as the draw liquor has to be exposed to the air before and during filtration, high temperatures of the liquor at the draw have been found to be undesirable. For the sake of keeping down ammonia losses as well as getting a high percentage sodium chloride decomposition in the brine, a draw temperature below 25° C. and even as low as 20° C. has been found beneficial. The point *K*, where the decomposition of NaCl reaches its maximum, is unique, furnishing a good guide for plant operation. This point moves toward the NH_4Cl-axis as the temperature rises above 15° C., according to the results of P. P. Fedotieff, and lies on the NH_4Cl-axis at about 32° C. Consequently, as the temperature rises above 15° C., the section of the curve *KM* dwindles in length. Therefore it might be correct to say that we are then operating around the point *K* on the $NaHCO_3$ side.

GRAPHICAL REPRESENTATION OF AMMONIA SODA PROCESS

We shall make use of triangular coördinates to represent the composition and solubility relationship in a more complex system such as the liquor and slurry in the ammonia soda process. This graphical representation has the advantage that it enables the reader to visualize the steps in the process more clearly. But before we present these diagrams it may be well to review briefly the properties of the triangular graphs. It is evident that triangular coördinates present to us plain curves. By adding a vertical coördinate—a fourth variable—a space curve is readily obtained in the body of a prism.

Let the triangle be an equilateral triangle *ABC*; each of the vertices represents a variable. In our present case, each of the three vertices may

represent a component in a solution or slurry. Thus, we may let A be Cl^-, B be OH^- and C be HCO_3^- as in Fig. 49 (b). Each side of the equilateral triangle represents molar percentage or fractions of a two-component system and its total length adds up to 100 per cent (from 0 to 100 per cent of one component and conversely from 100 to 0 per cent of the second component). Thus, point R in (b) represents 15 per cent OH^- and 85 per cent Cl^- on one side (AB), and point P represents 15 per cent OH^-, 55 per cent HCO_3^- and 30 per cent Cl^-. The three coördinates drawn parallel to
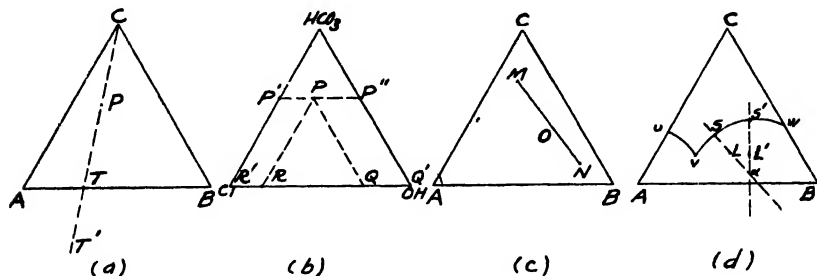
FIG. 49.   Triangular graphs.

the respective sides of the equilateral triangle in successive order are $R'R$, $Q'Q$ and $R'P'$, or $R'R$, QQ' and RP ($=RQ$). Therefore the following propositions may be readily proved:

(1) The sum of the three coördinates of a point in a triangular graph is a constant and is equal to the length of one side of the equilateral triangle, and each side may thus be graduated to read from 0 to 100 per cent of each of the two components.

(2) If M and N, Fig. 49 (c), represent the composition of two different solutions, the composition of a mixture of these two solutions mixed in any proportion is represented by a point on a straight line connecting M and N, such as O, and by no other point. Further, if O is the composition of the resulting mixture of the two solutions whose compositions are represented by M and N, MO then represents quantitatively (to scale) the quantity of the solution N and NO the quantity of the solution M present in the mixture.

(3) If P represents the composition of a system of three components, Fig. 49 (a), the removal or addition of one of three components is represented by points on the straight line connecting P and the vertex representing that component. Thus, in Fig. 49 (a), connect P and the vertex C, and produce CP to intersect the opposite side AB at T. Addition of component C to the system is represented by a point moving from P toward C; while removal of component C is represented by a point moving away from P along the line CP produced, and at T, component C is entirely eliminated, and the system then becomes a two-component one. AT then represents

the percentage of B, and BT the percentage of A in the resulting two-component system. Further, by taking points beyond T, such as T', we can conceive that T' represents algebraically a negative coördinate C in the three-component system. Suppose now C represents water in a solution, in which A and B are two solutes, addition of water (dilution of solution) is represented by a point moving from P toward the vertex C; while removal of water (concentration of solution) is represented by a point moving away from P toward T on the line CP produced.

(4) If in Fig. 49 (d) α represents the composition of a double salt in a system where C represents H_2O and uvw represents the solubility curve of the double salt at a certain temperature t, a straight line connecting any point, S, on this solubility (saturation) curve with α represents a mixture of the solid double salt and its mother liquor. If L represents such a mixture, the ratio of the weight of the double salt to that of the mother liquor present in the slurry is as $SL : \alpha L$. Further, if $S'L'$ represents the compositions of another slurry at different temperatures yielding a series of saturated solutions with the same double salt in the solid phase, the intersection point α between the two straight lines SL and $S'L'$ then determines the composition of the double salt α itself and thus locates it on the graph.

In general, as can be seen above, if a point P, representing the composition of a system, is to vary with respect to one component only, join P with the vertex of the triangle representing that particular component. Then any point on the line or on this line produced, represents the composition resulting from the variation of this one component alone, and consequently is a locus of constant ratio between the two components represented by the two remaining vertices.

Graphical representation of the ammonia soda process by means of a triangular prism is shown in Fig. 50. This process diagram is based on a system of triangular coördinates for OH^-, HCO_3^- and Cl^- with a fourth (vertical) ordinate for Na^+—NH_4^+ in the space relationship. Each edge of the prism is graduated to read from 0 to 100 per cent of one component or from 100 to 0 per cent of the other, and the six corners (or apices) represent respectively $NaCl$, $NaHCO_3$, $NaOH$, NH_4Cl, NH_4HCO_3 and NH_4OH. We have not considered H_2O, but represent these six components on the dry basis.

Let us start with brine at the $NaCl$ apex. Because of the presence in the salt of certain calcium and magnesium salts which upon ammoniation yield equivalent amounts of fixed ammonia (3-5 per cent as NH_4Cl), this point is represented not by the $NaCl$ apex but by A, along the edge $NaCl$—NH_4Cl. We ammoniate this brine in the absorber with ammonia gas from the distiller, cooled through the distiller condenser, containing about 0.2 mol CO_2 per mol of NH_3. In other words, this distiller ammonia gas is already about 20 per cent bicarbonated and is therefore repre-
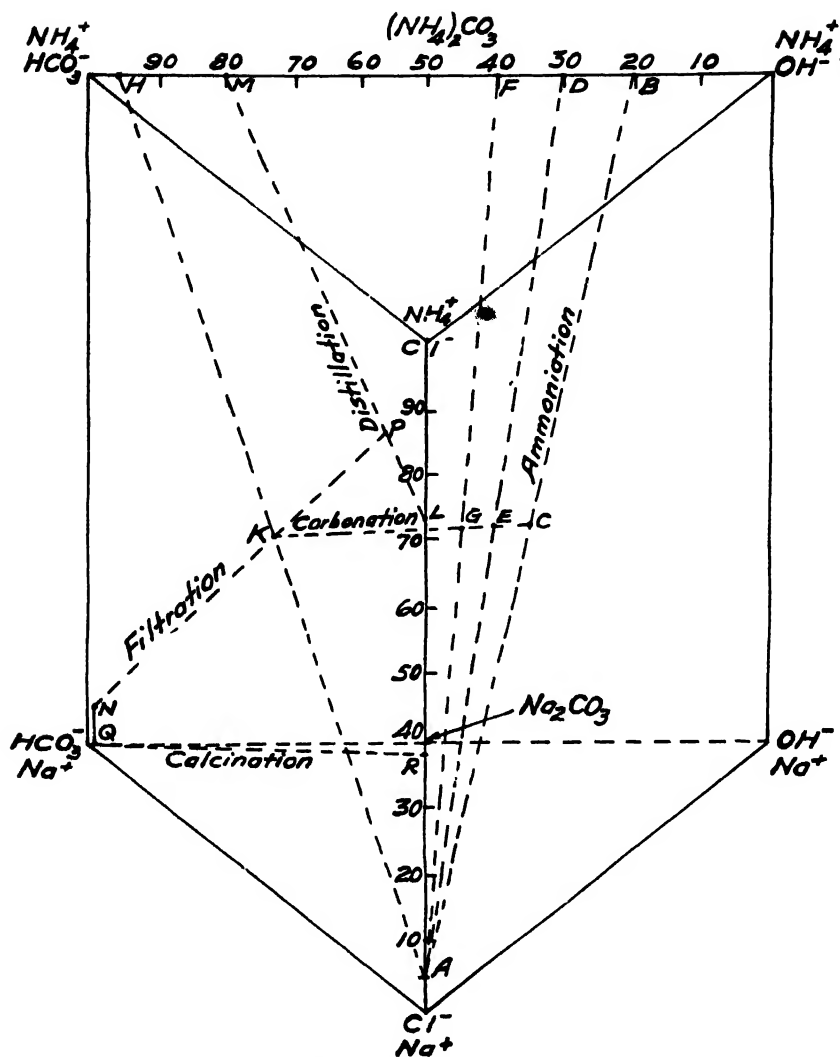
Fig. 50. Ammonia Soda Process Diagram.

(A) Crude brine (Ca and Mg impurities converted to fixed ammonia).
(B) Distiller gas to absorber (ammonia gas 20% bicarbonated).
(C) Ammoniated brine from absorber (about 99 NH₃ titer and 89 Cl titer).
(E) Pre-carbonated liquor from cleaning tower (below 32% bicarbonation).
(K) Draw slurry from making tower (about 95% bicarbonated).
(M) Ammonia gas liberated from top of heater (about 80% bicarbonated).
(L) Heater liquor to prelimer containing only fixed ammonia.
(N) Crude bicarbonate from filter containing NH₄HCO₃ and NaCl.
(R) Light ash from Rotary Dryer containing small amount of NaCl.

sented by B. Join A and B. As ammoniation proceeds, we arrive at C
where the titer of Cl is about 89 and that of ammonia 99, or when the
ratio of ammonia to sodium chloride in the ammoniated brine is as 1.11

to 1. This ammoniated brine, after settling and cooling, is pumped first to the cleaning tower where a small amount of lean CO_2 gas is passed in. The liquor is allowed to be carbonated in the cleaning tower to less than 30 per cent bicarbonation, or until it contains about 65 g CO_2 per l. This is represented by point E at the intersection of the carbonation line KC and the line AD connecting A with the 30 per cent bicarbonation point D. This precarbonated liquor is then sent into the making towers where it is finally carbonated to the highest degree possible. The carbonation line, KC, is not exactly parallel to the ammonia plane or NH_4HCO_3—NH_4OH edge, but is slightly inclined away from it on account of loss of ammonia gas from the ammoniated brine due to the stripping effect of the CO_2 gas in the towers.

Precipitation of $NaHCO_3$ gradually occurs in the making towers; for above about 32 per cent bicarbonation, the solubility product of sodium bicarbonate ($Na^+ \times HCO_3^-$) begins to be exceeded, and the precipitation commences long before the ammoniated brine reaches its maximum bicarbonation. Because of hydrolysis, it is not possible to get 100 per cent bicarbonation. In fact, precipitation of $NaHCO_3$ in the making tower takes place considerably at the 40 per cent bicarbonation point G, and continues as carbonation progresses until the maximum point K is reached at about 95 per cent bicarbonation, which occurs at the bottom of the making tower, where the richest CO_2 gas comes into contact with the liquor, and the magma is about to be drawn out. But, strange to say, the mother liquor in the magma in equilibrium with the bicarbonate crystals is still only about 82 per cent bicarbonated. The highest degree of bicarbonation, K, is at the point of intersection of the carbonation line KC and the line from A to H, the 95 per cent bicarbonation point.

The slurry at K is filtered, giving the filter liquor P and the crude bicarbonate (ammonia soda) N. Because of the presence of NH_4HCO_3 to the extent of 5 molal per cent in the crude bicarbonate, the line KN does not pass through the $NaHCO_3$ apex but some point N near it. Upon calcination, NH_4HCO_3 is driven off so that Q is reached. $NaHCO_3$ Q is then decomposed to light ash, R, which does not quite coincide with the middle point $Na\left(\dfrac{CO_3}{2}\right)$ or Na_2CO_3 of the $NaHCO_3$—$NaOH$ edge, as it should. Here again the calcination line QR does not exactly follow the $NaHCO_3$—$NaOH$ edge on account of the presence of some $NaCl$ as one of the impurities in the soda ash.

The filter liquor at P is first sent to the distiller heater and the "free ammonia" is decomposed, yielding about 80 per cent bicarbonated ammonia gas M, and a heater liquor L, containing about 72 per cent fixed ammonia (as NH_4Cl). This heater liquor flows into the prelimer and finally passes through the lime still giving rise to $CaCl_2$ in the distiller waste. The 80% bicarbonated heater gas is mixed with the ammonia gas from the lime still, coming over as 20% bicarbonated distiller gas to the absorber.

Chapter XIII

Decomposition of Sodium Bicarbonate by Calcination

The washed sodium bicarbonate from the filters drops onto a belt conveyor which feeds the furnaces in which the bicarbonate is decomposed by calcination. The bicarbonate is charged into the furnaces through star feeders, or better still, by feed tables whereby a good air seal is secured, so that air may not be drawn into the furnaces with the bicarbonate feed nor the furnace gas blown out.

The reaction in the furnace is the decomposition of sodium bicarbonate into soda ash, carbon dioxide and water. The process looks very simple, and it is so in a laboratory where the product can be stirred and no attempt is made to recover either ammonia or CO_2 gas and this CO_2 in a concentrated form.

But in actual operation it is one of the most difficult parts of the whole process. Difficulties in this operation have brought much trouble to the project, and plants have failed because this particular part of the process has not been successful. The difficult nature of this operation can be judged from the number of patents which have been issued on the apparatus invented to perform it. For it is not simply a drying operation. The whole difficulty arises from the following facts: (1) Sodium bicarbonate has a tendency to cake into lumps or balls, especially when its moisture content is high, these lumps having undecomposed bicarbonate cores which heat can hardly reach from the outside. (2) The wet sodium bicarbonate forms a hard scale on the surface of the steel shell through which heat cannot penetrate, and consequently the localized heat is likely to burn out the metal. (3) The dried ash has a great avidity for the steam condensate and becomes "set," plugging such passages as the return ash chute, the extract barrel, etc., if the steam is not conducted away fast enough, *i.e.*, if the dryer happens to be under pressure. In addition, it is necessary to get a bicarbonate-free soda ash, to lose little or no ammonia or CO_2 gas, and finally to maintain a high CO_2 concentration in the returned gas.

In the early days, an enclosed dishpan, 10 to 14 feet in diameter, provided with a stirrer, and an opening in the cover for gas outlet, was used. This, of course, did not give continuous operation. In 1882, Striebeck introduced into the ammonia soda industry the Thelen pan in a somewhat modified form, which had been used successfully in the LeBlanc soda industry. From that time on, this type of pan superseded older types of calcining apparatus. Even today some are still in use in Europe. It was also customary to divide the calcining operation into two stages, one

a preliminary drying operation and the second a finishing operation. The former involved driving out moisture, ammonia, and a large part of the CO_2 (about 75 per cent), while the latter drove off the rest of the CO_2 and completed the operation. The preliminary operation was carried out either in the dishpan or in a lightly fired Thelen pan, and the partially calcined bicarbonate was finally finished off in the finishing Thelen pan. It is claimed that a denser soda ash was obtained this way. One construction of Thelen pan consisted of 6 cast-iron semi-circular sections, 7 feet in diameter, $1\frac{1}{4}$ inches thick and 5 feet 4 inches long, each pan being 32 feet long. The cover consisted of convex wrought-iron plates. A series of cast-steel scrapers inside was actuated by a common shaft which oscillated through an angle of about 90°. Openings for bicarbonate charge and gas outlet were provided in the cover at the front near the furnace end. The ash extract was located at the rear end in the bottom of the shell below the pan. A Thelen pan, 7 feet in diameter and 34 feet long, has a capacity of 20 tons of ash per 24 hours, and requires coal consumption of about 3 tons, and power consumption of 10 to 15 hp. It is thus seen that fuel economy in the Thelen pan is excellent, and the ash obtained generally somewhat denser. It can be arranged so that no returned ash is required in the Thelen pan calcination, thus obtaining good fuel economy.

The ash made by the ammonia process is very loose and light. It takes more packing space and a larger bag per unit weight than the LeBlanc ash. Hence there is a heavier packing cost per unit weight of ash. In a number of industries this light powder is not in favor, especially in the glass and ultramarine industries. This is a distinct disadvantage for the ammonia process as against the LeBlanc process. In earlier times, this was overcome by subjecting the ash again to an open fire in a gas-fired reverberatory furnace. The ash was thus brought to a state of incipient fusion and became densified. If the calcining operation was carried out in two stages, the partially decomposed bicarbonate, or "roaster ash," was best utilized for this dense ash making. This was done either in a revolving furnace like a black ash revolver, or in the Mactear mechanical furnace which had been in use in the LeBlanc industry since 1876. The latter is a type of reverberatory furnace having a circular, horizontal revolving fire-brick bed as large as 20 feet in diameter. The "roaster ash" was dumped onto this horizontal bed and the charge was turned over continuously by a number of small revolving stirrers rotating about axes stationary with respect to the revolving bed. When the operation was completed, the dense ash was scraped out through a central opening at the bottom of the revolving bed. This is thus a batch process.

The apparent density of the ammonia soda ash varies according to the manner in which it is determined. The apparent density of the normal ash, or light ash, when loosely packed, is about 0.5, *i.e.*, almost 500 grams per liter. When the same ash is well shaken in a cylinder and tapped until no more diminution in volume is observed, the apparent density becomes approximately 0.7. Similar differences exist in the case of a

dense ash. A dense ash of 0.9 to 1.0 apparent density when loosely filled, will give a value of 1.2 to 1.3 when thoroughly shaken down. By the densifying process described above, the ash volume is contracted under heat and the density can be made equal to that of the LeBlanc ash. From a poorer grade of bicarbonate crystals having a lower yield, the ash obtained may be denser, and conversely.

The practice of dividing the calcining operation into two stages and of making dense ash by the fire method described above is now obsolete. In the United States none of the equipment described above was in use to any great extent in the ammonia soda industry except possibly some Thelen pans in the Columbia Alkali Corporation.

In America in the early days, calcining of the wet crude bicarbonate (ammonia soda) which has a slight amount of salt and ammonia, was at first done in shallow pans having revolving knives supported from the cover. The moist bicarbonate was shovelled into a side door and, after being heated by the fire below to a temperature of 180° C., a part was drawn out with a hoe, leaving enough to mix with the wet charge to prevent scaling of the pan. These "secheurs" were not efficient. Air leaked in and CO_2 and ammonia gases escaped, so that the CO_2 in the gas was not much over 60 per cent and considerable ammonia was lost.

The next development was rotary cylinders some five feet in diameter and 60 feet long, revolving inside a furnace on tires supported on wheels at the ends. These cylinders were later changed to cylinders 6 feet in diameter, driven by gears, at first with steam engines and afterward with motors. These are the prototype of the present rotary calciners so universally used in American ammonia soda plants. Improved feed tables and feed screws were devised to mix the returned ash with the charge in order to reduce the moisture to about 6 per cent to avoid scaling of the cylinders. Improved furnace design and automatic stokers have made these rotary calciners efficient machines in performing this difficult operation.

The rotary dryer has been developed to a high degree of perfection in America. It possesses many advantages over the European soda ash roasters, including the Thelen pans. It has a larger capacity and less power consumption per unit of output. It is capable also of giving a high-test returned gas. Formerly the shell was riveted (butt-strap joints); now these shell joints are either electrically welded or forged. The present standard machine is 6 feet in inside diameter and 62 feet in over-all length. The body of the cylinder is made of $\frac{7}{8}$-inch steel plates (20 × 20 feet or 20 × 10 feet sheets). The joints in the body are best forged together, or else are V-ed at 75° or 60° both outside and inside for electric welding, and the welded seams inside the shell ground smooth. In electrically welded cylinders the girt-welded seams must be staggered to avoid continuous joints. The two end sections are of cast steel or cast iron, conical in shape, 6 feet inside diameter at the larger end, 5 feet at the smaller end, and 5 feet long each, riveted to the ends of the steel cylinder body. The whole kiln is enclosed inside the brick setting with

the exception of a part of the conical heads at both extreme ends. The kiln is supported at the extreme ends on two pairs of rollers. The girt gear is attached to the extract end just outside of the brickwork. The tires at both ends and the four rollers are made of cast steel. The dryer runs at about 4 r.p.m. The kiln is supported in a horizontal position. Bicarbonate is charged in through a feed table and the dry ash from the returned ash screw conveyor is fed to the feed barrel at the front end, mixed with the wet bicarbonate by a feed screw, and conveyed into the furnace by a ribbon conveyor. The gas uptake is located at the feed end just behind the feed inlet pipe and the ash is extracted by means of a screw conveyor at the opposite end. The furnace is located at the feed end so that this arrangement of heating is not counter-current. Throughout the length of the dryer, dragging along at the bottom inside is a C.S. scraper chain with hardened steel blades attached to the links to keep the shell free of soda scales. The chain is fastened to a fixed-feed support at the feed end and to the extract barrel at the extract end. The ash from the extract barrel discharges to a screw conveyor called the "collecting conveyor," is cooled in an ash cooler, and finally goes to the packing bin through a rotary screen of 4 to 8 mesh. The screened ash is packed in double gunny bags holding 200 lbs. or 90 kilograms per bag. A portion of the unscreened ash is diverted to the returned ash conveyor to be fed back to the dryers as returned ash mentioned above. Tailings from the screen are sent back to the dryers with the returned ash. When the bicarbonate crystals are normal, very few lumps are formed in the soda ash from the dryers and the amount of such tailings is very small. The amount of the returned ash employed depends entirely on the dryness, or the "yield," of the bicarbonate from the filters. This in turn is determined by the crystalline character of the bicarbonate obtained from the columns. Good filters working on good bicarbonate crystals should give a yield of 53 to 55 per cent or 12 to 13 per cent H_2O as free moisture on the weight of the filter bicarbonate. Sodium bicarbonate as obtained from the filters is too wet to be fed to the dryers alone (*i.e.*, without a proper amount of returned ash) and would form hard scale and lumps in the dryers, causing serious difficulties. The returned ash mixed in the wet bicarbonate brings down the moisture percentage in the aggregate and consequently causes the bicarbonate to dry to a loose powder, forming little or no scale on the shell of the dryer. The necessity of feeding back the dry ash with the bicarbonate naturally cuts down the capacity of the dryer and also lowers the heat efficiency. In practice, a limited quantity, and no more, of the returned ash is employed which will just eliminate scaling in the dryers.

Rotary cooling conveyors with inside spirals deliver cooled ash to screens and packing bins, from which the ash is either packed in bags by means of screw packers, or loaded by means of pneumatic conveyor into enclosed railway cars and shipped in bulk, or conveyed into great concrete silos from which it can be retrieved by conveyors, as the case may be.

The brickwork for the rotary furnace, as in steam boiler setting, requires considerable study and experience. The space for the combustion chamber, the relative height and location of the bridge wall, and the spaces allowed under and around the shell for flue passage are the results of close study and observation. Other conditions being equal, *i.e.*, with a given grade of bicarbonate crystals and a given grade of coal, these considerations and the grate area of the furnace determine the drying
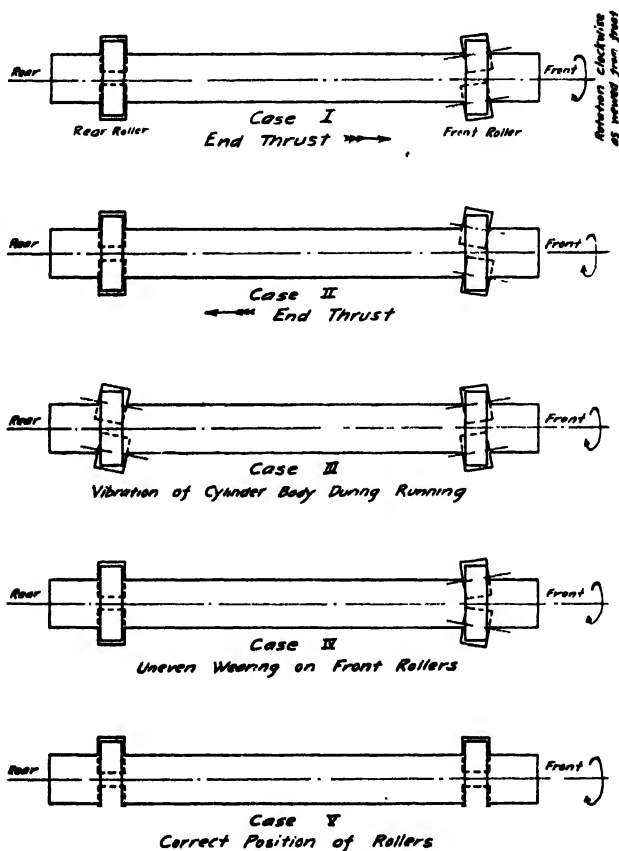
FIG. 51. Position of axes of rollers with respect to axis of cylinder.

capacity of the dryer. A standard six-foot-diameter rotary dryer has a capacity of 50 to 60 short tons of soda ash per 24 hrs. The power required to drive the rotary dryer at 4 to 5 r.p.m. is 15 to 20 hp. But the capacity of a dryer is largely dependent upon the crystalline character of the bicarbonate. A 72-inch by 60-foot rotary dryer working on a coarse-grained dry bicarbonate will turn out 55 tons of soda ash per 24 hours with ease, whereas the same machine working on a wet bicarbonate with poor crystals operates with difficulty at the rate of 30 tons of soda ash

a day. At present, there is a tendency to build larger rotary dryers, 8 feet or more in inside diameter and 80 feet long, using steel plates 1⅛ inches thick, all of welded construction.

In this connection it may not be out of place to point out the effect of the central line position of the shafts of the rollers on the behavior of the dryer cylinder. A rotary cylinder, be it a rotary soda dryer, a rotary lime slaker, or a rotary lime kiln, supported at two points on two pairs of rollers, one pair at each end, is frequently found to have a persistent tendency to creep forward or to recede while it is running. This end thrust is sometimes so great that it causes the flanged tires or guide rollers (whichever method is used to take care of the axial thrust) to

TABLE 80. Progress of Calcination of Crude Sodium Bicarbonate at 160° C

Time Min.	Na_2CO_3	$NaHCO_3$	NaCl Per Cent	NH_4HCO_3	H_2O
0	6.68	76.04	0.45	3.09	13.74
20	17.07	78.04	0 70	1.28	3.92
30	19.61	76.19	0.76	0.73	2.71
35	34.13	63.33	0.76	0.33	1.45
45	67.89	30.07	0.86	0.10	1.08
50	93.68	5.18	0.93	trace	0.21
55	99.09	nil	0.93	nil	nil

TABLE 81. Progress of Calcination of Crude Sodium Bicarbonate at 175° C.

Time Min.	Na_2CO_3	$NaHCO_3$	NaCl Per Cent	NH_4HCO_3	H_2O
0	6.68	76.04	0.45	3.09	13.74
15	21.94	75.52	0.78	1.10	0.66
20	30.79	67.20	0.82	0.62	0.57
25	60.42	38.22	0.87	0.29	0.20
35	96.24	2.79	0.91	nil	nil
40	99.20	nil	0.92	nil	nil

TABLE 82. Progress of Calcination of Crude Sodium Bicarbonate at 190° C.

Time Min.	Na_2CO_3	$NaHCO_3$	NaCl Per Cent	NH_4HCO_3	H_2O
0	6.68	76.04	0.45	3.09	13.74
15	35.09	62.99	0.87	0.56	0.49
20	45.53	53.05	0.88	0.24	0.30
25	71.42	27.70	0.90	trace	nil
30	97.31	1.84	0.89	nil	nil
35	99.10	nil	0.92	nil	nil

* S. T. Kuo, Thesis, Chemical Engineering Department, Purdue University, 1932.

wear out very fast, with serious results. Experience has shown that this end thrust is caused by the axes of the rollers (roller shafts) not being placed parallel to the axis of the cylinder shell (or square to the surface of the cylinder tire). Careful reasoning will make it evident that in Case I (Fig. 51) the cylinder will tend to creep forward and in Case II the cylinder will tend to creep backward, if the rotation in each case is clockwise as viewed from the front. Reversing the direction of rotation in each case reverses the direction of the thrust. This occurs regardless of whether the cylinder body is placed horizontally or inclined toward

the back end or toward the front end. Conditions shown in Case III, where two rollers in one pair are set in the opposite direction to the other will not produce any axial thrust in the cylinder; nor will conditions shown in Case IV, where one roller in a pair is set in the opposite direction to the other. Conditions shown in Case III may cause the cylinder body to vibrate while running. In any case where the axis of a roller is

TABLE 83. Progress of Calcination of Crude Sodium Bicarbonate at 205° C.*

Time Min.	Na_2CO_3	$NaHCO_3$	NaCl Per Cent -	NH_4HCO_3	H_2O
0	6.68	76.04	0.45	3.09	13.74
15	52.26	46.07	0.93	0.42	0.32
20	78.96	19.72	0.90	0.18	0.24
25	97.94	1.07	0.93	trace	nil
30	99.05	nil	0.91	nil	nil

* S. T. Kuo, Thesis, Chemical Engineering Department, Purdue University, 1932.

not placed parallel to that of the cylinder body, one end of the roller face will bear on the cylinder tire harder than the other, and that end will wear down more rapidly. If all rollers are placed square to the tire with roller shafts parallel to the axis of the cylinder body, the cylinder shell will run very steadily and no axial thrust one way or the other will be thrown on the guide flanges or guide rollers. The behavior of a rotary cylinder described above can be explained on the same principle as the motion of a boiler tube expander shaft when a.mechanic turns the shaft of the expander inside a boiler tube at the tube sheet.

In the dryers, free moisture is first driven out; ammonium bicarbonate is then decomposed and its constituents, ammonia, carbon dioxide and water, are also driven out. The sodium bicarbonate is only slowly decomposed and the last portion is decomposed with some difficulty. The following determinations in Tables 80-88 were made in a small, electrically heated rotary oven on a commercial sample of crude sodium bicarbonate from the filters and also on a sample of C.P. sodium bicarbonate for comparison. The gases were vented to the air and in the case of the crude sodium bicarbonate the charge was also mechanically crushed to prevent caking.

The following are data on C.P. sodium bicarbonate:

TABLE 84. Progress of Calcination of C.P. Sodium Bicarbonate at 140° C.*

Time Min.	Na_2CO_3	$NaHCO_3$ Per Cent	H_2O
0	5.50	91.48	3.02
10	6.62	90.64	2.74
20	9.91	88.96	1.13
25	18.60	80.80	0.60
30	25.31	74.72	nil
35	59.41	40.55	nil
40	69.32	30.65	nil
45	78.12	21.92	nil
50	92.43	7.90	nil
55	98.64	1.39	nil
60	99.97	nil	nil

* S. T. Kuo, Thesis, Chemical Engineering Department, Purdue University, 1932.

TABLE 85. Progress of Calcination of C.P. Sodium Bicarbonate at 160° C.*

Time Min.	Na_2CO_3	$NaHCO_3$ Per Cent	H_2O
0	5.50	91.48	3.02
5	8.80	89.80	1.40
10	20.93	79.37	nil
15	31.91	68.03	nil
20	64.93	34.86	nil
25	82.57	17.44	nil
30	99.06	0.87	nil
35	100.04.	nil	nil

TABLE 86. Progress of Calcination of C.P. Sodium Bicarbonate at 175° C.*

Time Min.	Na_2CO_4	$NaHCO_3$ Per Cent	H_2O
0	5.50	91.48	3.02
5	9.90	88.95	1.15
10	39.62	61.00	nil
15	65.13	34.84	nil
20	99.05	0.96	nil
25	100.10	nil	nil

TABLE 87. Progress of Calcination of C.P. Sodium Bicarbonate at 190° C.*

Time Min.	Na_2CO_3	$NaHCO_3$ Per Cent	H_2O
0	5.50	91.48	3.02
5	15.41	84.60	nil
10	40.70	60.04	nil
15	87.50	12.48	nil
20	100.09	nil	nil

TABLE 88. Progress of Calcination of C.P. Sodium Bicarbonate at 220° C.*

Time Min.	Na_2CO_4	$NaHCO_3$ Per Cent	H_2O
0	5.50	91.48	3.02
5	40.28	59.88	nil
7.5	78.55	21.42	nil
10	98.13	2.00	nil
12.5	100.10	nil	nil

* S. T. Kuo, Thesis, Chemical Engineering Department, Purdue University, 1932.

In the decomposition of the bicarbonate one difference is to be noted, and that is the factor of the composition of the vapor phase in contact with the bicarbonate. If the gases are vented to the air as in the laboratory experiments, the gas phase may contain different concentrations of CO_2 and H_2O from those in the closed system in actual operation, and proper allowance should be made regarding this point in the interpretation of the results. As can be seen from the decomposition of C.P. $NaHCO_3$, complete decomposition of the bicarbonate is not only a function of temperature but it is also a matter of time (duration). It will be seen that at or above 175° C. the order of the completion of decomposition is: First the free moisture in the bicarbonate, then the ammonium bicarbonate, then the decomposition of the bulk of the sodium bicarbonate, and
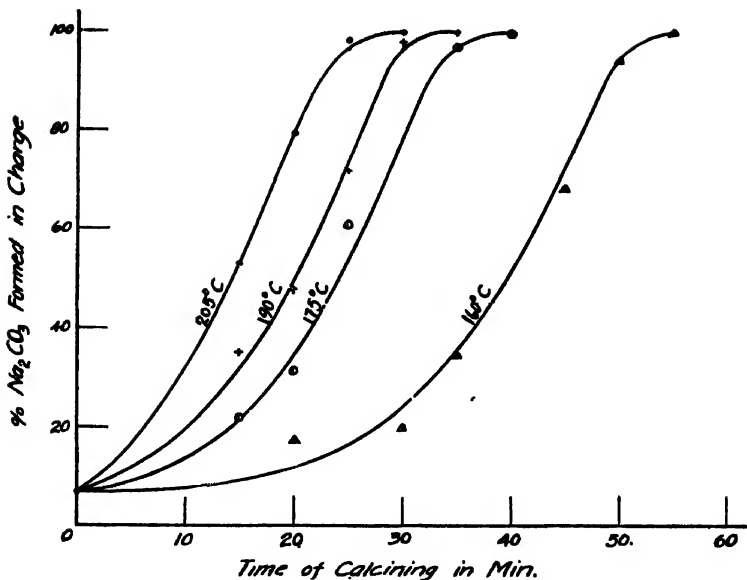
FIG. 52. Curves showing progress of calcination of crude
sodium bicarbonate from filters.
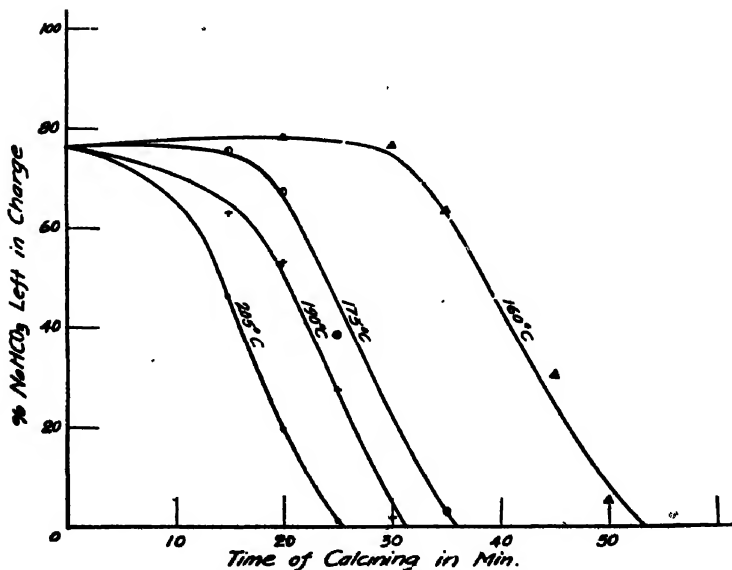
FIG. 53. Curves showing progress of calcination of crude
sodium bicarbonate from filters.

finally the last portion of sodium bicarbonate, the last trace of sodium bicarbonate in the ash being rather difficult to decompose completely.

Curves showing the increase of sodium carbonate, the decrease of sodium bicarbonate, the decrease of ammonium carbonate and the decrease of moisture with time during calcination at different temperatures are plotted in Figs. 52, 53, 54, 55, 56, and 57. These temperatures are selected as representing the whole range of the ash extract temperatures
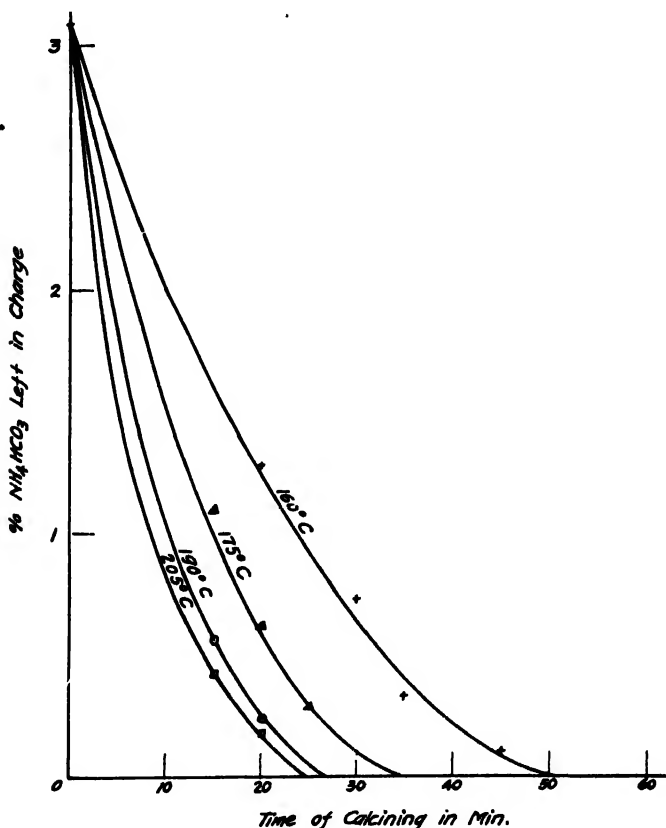
FIG. 54. Curves showing progress of calcination of crude sodium bicarbonate from filters.

in the operation of rotary dryers. It is seen from these observations that at 160° C. the crude bicarbonate can be completely decomposed, but it requires a longer time than at higher temperatures. This is borne out in practice, for it is found that at 160° C. extract temperature, the ash can be completely freed from bicarbonate provided that it is allowed to remain in the furnace for a sufficient time. At a high rate of operation, whereby the time is greatly reduced, a higher extract temperature (minimum 175° C.) is maintained to insure complete decomposition of the

bicarbonate. The best working extract temperature may be said to lie between 175° and 190° C.

Chemically the decomposition reactions are as follows:

$$NH_4HCO_3 \rightarrow NH_3 + CO_2 + H_2O$$
$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

Any ammonium chloride in the filtered bicarbonate will be converted to sodium chloride, a reaction representing the reverse of the tower reaction.

$$NH_4Cl + NaHCO_3 \rightarrow NaCl + NH_3 + H_2O + CO_2$$
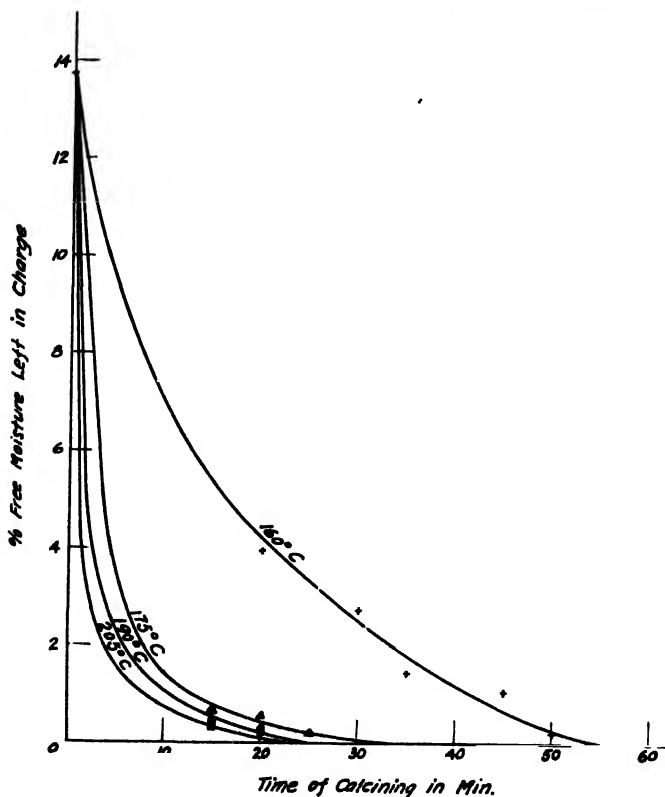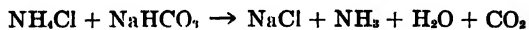
FIG. 55. Curves showing progress of calcination of crude sodium bicarbonate from filters.

The sodium chloride formed this way, together with that carried in the mother liquor left in the wet bicarbonate, constitutes the total sodium chloride in the finished ash. Any incompletely settled mud in the ammoniated brine fed to the towers would show in the soda solution as a turbidity or precipitate. The insoluble matter in the ash made from the ammonia process is generally magnesium carbonate and ferric oxide (Fe_2O_3). Any hardness in the wash water used on the filters adds to the
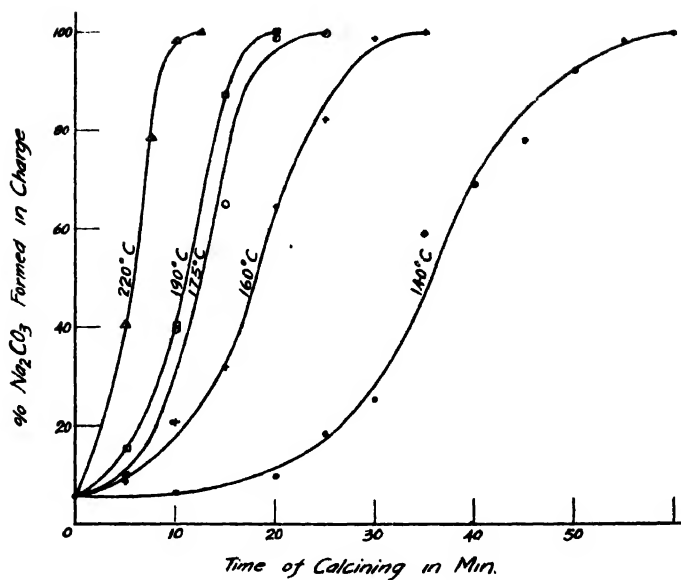
FIG. 56. Curves showing progress of calcination of
C. P. sodium bicarbonate.
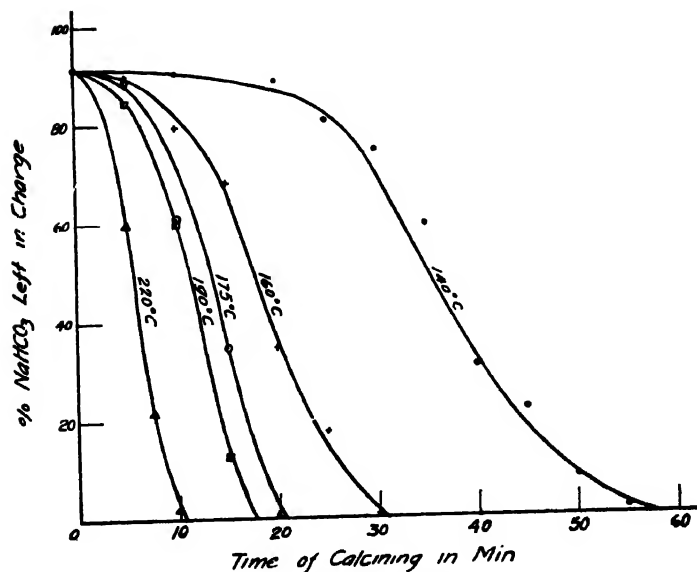
FIG. 57. Curves showing progress of calcination of
C. P. sodium bicarbonate.

insoluble content of the ash (as $CaCO_3$ and $MgCO_3$). The bicarbonate carries some iron rust from the towers and from the ammoniated brine fed to them. All iron will be converted to Fe_2O_3 in the furnace, although in some abnormal cases where there is too large an excess of sulfide in the ammoniated brine, the iron may appear as the gray FeS in the ash extracted from the dryers; but it gradually turns brown later on exposure to the air. Sometimes little brown particles containing iron may be discovered in the ash. The yellowish-red appearance of the product is due to Fe_2O_3 present in the ash, and its color is very much intensified by having a soft paste made of the ash with a little water. A simple and quick test for the quality of the product is to dissolve 15 grams of the ash in 100 cc. of distilled water and to examine the solution for any turbidity or precipitate and for any reddish or yellowish coloration developed in the solution. A specification of ammonia ash of salable quality is given in Table 89.

TABLE 89.   Minimum Standard of Purity in Ammonia Soda Ash.

1. Na_2CO_3	....	$> 98.5\%$
2. $NaHCO_3$	....	— None or a very small fractoin
3. NaCl	....	$< 0.8\%$
4. Na_2SO_4	....	$< 0.05\%$
5. Fe_2O_3	....	$< 0.003\%$
6. Insoluble matter	....	$< 0.05\%$
7. Solution	....	— Colorless and clear, free from black, gray or red particles and from any ppt.
8. Water absorbing power	.....	— 135% on the weight of ash

The above specification applies to fresh ash only, which has not been kept in storage for any length of time. Old ash may have absorbed moisture and CO_2 from the air to such an extent that the sodium bicarbonate content would be much greater and the water-absorbing power less. A good grade of ammonia soda ash should have the composition shown in Table 90.

TABLE 90.   Analysis of a Good Grade of Ammonia Soda Ash.

1. Na_2CO_3	....	99.5%
2. $NaHCO_3$	....	nil
3. NaCl	....	0.3%
4. Na_2SO_4	....	0.02%
5. Fe_2O_3	....	0.002%
6. Insoluble matter	....	0.03%
7. Solution	....	Clear and colorless
8. Water absorbing power	....	135-140% on the wt. of the ash taken

Again, such results are obtained only in samples taken fresh from the furnace or from samples that have been recalcined in the laboratory to remove moisture and CO_2. It is frequently reported that soda ash from the furnace contains caustic soda to the extent of 0.1 to 0.2 per cent. This seems to be not incompatible, especially when the bicarbonate fed is wet and the temperature in the furnace is abnormally high.

The whole secret of dryer operation lies in having a proper amount of returned ash. It is of course impossible to ascertain just what the exact ratio must be between the weight of the dry ash returned to the furnace and that of the bicarbonate fed at any moment. This could only be ascertained by observing the character of the ash extracted, by the shell condition inside, and by the temperature of the ash so extracted. If the returned ash is deficient, the shell would tend to form scale, the extracted ash would contain balls or lumps, and, as a rule, the shell expansion would be excessive. Under these conditions the shell is likely to become overheated, and in serious cases the forged joints or the electrically welded seams may crack and the cylinder shell fail. On the other hand, if the returned ash is sufficient for the rate of bicarbonate feed, the ash would be practically free from balls and come out loose and dead like flour meal, only somewhat coarser. The grains would be loose, but not light and "flowing," as when the ash contains much undecomposed bicarbonate. The temperature of the extract then can be maintained above a point where all the bicarbonate is completely decomposed and the extraction of the ash from the dryer can continue practically without interruption during the 24 hours. The shell would be clean and its expansion reduced to a minimum for the quantity of the output. The quantity of the returned ash varies as the wetness of the bicarbonate: the lower the yield, the more returned ash is required for a given rate of the bicarbonate feed.

When the bicarbonate crystals are poor, the bicarbonate from the filters is wet and the drying operation becomes exceedingly difficult. With a modern filter and fair bicarbonate crystals from the tower (3 to 4 minutes test), a yield of 51 to 54 per cent is not a difficult matter. Anything above a 50 per cent yield, however, is fair. Very wet bicarbonate (say 28 per cent moisture) could be dried if a large excess of the dry ash is taken with it. This amount of returned ash, however, decidedly cuts down the capacity of the dryer and raises the fuel ratio required. Table 91 gives a rough guide as to the amount of returned ash required on the weight of the crude bicarbonate charged into the furnace.

TABLE 91. Approximate Amount of Returned Ash Required.

Free Moisture in Bicarbonate	"Yield" — Per Cent	Returned Ash Required for Drying
15	52	100
8	57½	40
4	60	Little or none

When the ash is to be packed as it is produced, the ash should be packed as hot as the bag can stand to avoid absorbing moisture from exposure to the air; a temperature of about 80° C. is favorable. Hot ash from the furnace can be air-cooled in sections of long screw conveyors generally constructed across the building. Sometimes it is carried to the top of the building and down to give a long path for air-cooling. If an ash cooler is desired, cooling can be carried out in a rotary cooler consist-

ing of a steel cylinder of about 5 feet inside diameter and 25 to 30 feet long fitted at both ends with cast-iron conical sections, through one end of which a screw conveyor carries in hot ash and from the other end another extracts cooled ash. The cooler is inserted in conveyor lines in a horizontal position, using angle-iron sections riveted to the shell inside to carry the ash forward. The discharge end of the cooler is provided with scoops which pick up the ash and feed it to the exit screw conveyor. The cooler is supported on rollers at the extreme ends, the arrangement being much the same as in a rotary dryer. The shell revolves in a basin of cooling water and the heat is carried away by evaporation in the same manner as in surface cooling. Soft water should be used in the basin; otherwise the cooler surface will be completely coated with hard scale, resulting in poor heat conduction. Frequently a cylindrical section of a rotating cooler is air-cooled and forms a part of the conveyor system located outside the building.

The rotary dryer is best operated under neutral conditions, *i.e.*, without pressure or vacuum. The gas main is provided with an automatic butterfly valve regulated by suction in the main, and this can be set by a counterweight to give an exactly neutral condition in the dryers. Too much vacuum would let air leak in, giving a low gas test. Too high a positive pressure makes the gases and steam blow out through the feed and extract openings with losses of CO_2 and ammonia, and would cause steam to condense in the feed barrel and returned ash chute, giving rise to a troublesome plugging. To avoid dilution of CO_2 by air, the extract barrel and returned ash chute should run full to secure a proper "seal," so that no space is left for air to be drawn in. Another place where air leakage may occur is in the bicarbonate feed opening. With a feed table of good design, the leakage can be practically eliminated. Butterfly valve packings, dryer neck packing ring, and barring holes provided for chiseling off furnace scale are sometimes also sources of air leakage. To get a high gas test from the dryer requires great effort and continued vigilance on the part of the operators. In the old days returned gas tested only 25 to 30 per cent CO_2. With the introduction of the Thelen pan, 60 to 80 per cent CO_2 test was considered very good. In rotary dryers it is now possible to get a 90 per cent gas test with no great effort. A rich gas from the furnace is worth a great deal to the works, for upon this depend the formation of good bicarbonate crystals, the high decomposition of NaCl in the towers, and the capacity of these towers (*i.e.*, the output of the plant).

The outlet gases containing ammonia, CO_2, and steam, together with the mechanically entrained soda dust, are first drawn by the suction of CO_2 compressors (which at the same time are taking kiln gases through a second branch of piping to form the mixed gases for the tower operation) through a scrubber called the furnace gas scrubber, to dissolve out the soda dust and a part of the ammonia and incidentally to cool the hot gases; then through a set of surface condensers with a large number of cast-iron cooling tubes, called the furnace gas condensers, to condense the steam; and finally through a scrubbing tower filled with coke or tiles

to scrub out the ammonia in the gas and to cool the gas. The gas then enters the CO_2 compressors free of ammonia, and cool (and consequently also dry). The filter liquor is used in the furnace gas scrubbers to scrub the soda dust, whence it goes to the distiller, incidentally having been preheated by the furnace gases for the distiller operation. The condensate from the furnace gas condensers containing strong ammonia and CO_2 drains to the filter liquor main on its way to the distiller. Good, soft water is used to scrub ammonia in the final scrubbing tower, and this wash water is then used on the filters to wash sodium chloride from the bicarbonate.

Normally, light ash has a bulk density (by the loosely-packed method) of above 0.540 (density of water equals unity). But this property has a great bearing on the condition of the column operation as regards the proper ammonia and chlorine titers in the green liquor fed to the columns and the richness of the CO_2 gases passed to the columns. For instance, in one case where the chlorine titer in the ammoniated brine fell from **89-90** to **85-86** (ammonia titer normal, **96-97**) because of accidental leakage of water into the absorber at its cooling box, the density of the ash obtained was reduced to 0.464. In another case where the gas to the columns was diluted by accidental opening of the kiln main for cleaning, the density of the ash obtained was only 0.508. With a low ammonia or chlorine titer, or both, in the ammoniated brine, or with a weak CO_2 gas in the columns, bicarbonate crystals formed in the columns would be finer and the bulk density (apparent density) of the soda ash obtained would be also lowered.

The density of soda ash depends on the physical state of aggregation. It is found that soda ash absorbs water and has a tendency to become "set" or conglomerated, *i.e.*, to form crystals of the monohydrate, $Na_2CO_3 . H_2O$. If then water is again driven out, the conglomerate structure remains. Hence the present method of making dense ash is by adding about 16 per cent water to the ash, mixing thoroughly in a screw mixer, and drying the mass again in a rotary dryer. The amount of water added corresponds roughly to the formation of the monohydrate, $Na_2CO_3 . H_2O$, and the conversion of the light ash to the monohydrate crystals explains the fact that the light ash becomes granular and densified. It is found that, to obtain the desired density, one-half of the densified ash should be fed back with the light ash in the dense ash furnace in the same way as the returned ash in the light ash dryers. The rotary type of dryer is very suitable for this work and has an even greater capacity on dense ash making. The outlet gas (which contains steam and a small amount of air) is drawn through a surface condenser by an exhauster, discharging it to the air. The steam condensate is used over again in the light ash feed. The density of the ash is brought up to 0.95 to 1.0 (loosely packed). This dense ash, therefore, is also called "water ash." The dense ash, especially the granular dense ash, is favored by glass manufacturers, because it possess advantages over the light variety in that

(1) it gives larger charging capacity for the melting pots, (2) it gives a longer time for reaction, and (3) it causes less dust loss.

In operating the dense ash furnace, the extract temperature should be maintained at 135° to 155° C. It should not be permitted to rise above 160° C., or the density of the ash obtained may fall. The screw conveyor system used for conveying the dense product must be arranged so that it is as short as possible to avoid any unnecessary grinding action on the dense ash particles. The dense product is then passed through a hummer screen to grade the different sizes for packing.

It was noted above that in order to insure complete decomposition of sodium bicarbonate the temperature of the ash extract must be maintained between 175° and 190° C. The temperature in the front of the dryer is of course much higher. A temperature of 270° C. is commonly given for the complete decomposition of $NaHCO_3$. Gautier [*Ber. deut. chem. Ges.*, **9**, 1434 (1876)] found that at 100° to 110° C. decomposition of sodium bicarbonate could go to completion. But this, of course, is a matter of time as noted above, and is also dependent upon the rate of removal of CO_2 and water. In practice, under good working conditions of the dryer, the gas obtained from the dryer main is over 90 per cent CO_2; and the partial pressures of CO_2 and water in contact with the solid bicarbonate inside the dryer are probably around 0.25 and 0.65 atmosphere respectively. The flue gases at the tail end of the furnace are usually at 350° to 450° C., depending upon the furnace setting and the draft which the furnace carries.

In the dryer reaction

$$2NaHCO_3 (solid) = Na_2CO_3 (solid) + CO_2 (gas) + H_2O (gas)$$

$NaHCO_3$ and Na_2CO_3 being in the solid phases,

$$P_{CO_2} \times P_{H_2O} \text{ (expressed in atm.)} = \text{constant at a given temp.}$$
$$= 0.23 \text{ at } 100° \text{ C.*}$$

Theoretically, there are three phases (two solid phases and a vapor phase) and three components (Na_2CO_3, CO_2, and H_2O), and the system is therefore bivariant. That is to say, the equilibrium depends not only upon the temperature but also upon the composition of the vapor phase (molal concentrations of CO_2 and water vapor). With wet bicarbonate there may be also a solution phase, and as long as the water (free moisture) is present in the bicarbonate this solution phase remains. Then, according to the phase rule, this system would be univariant. Since the decomposition can take place only when the product of the partial pressures of CO_2 and of water vapor in the vapor phase is less than a certain value (such as 0.23 at 100° C.), it is easily seen that when the bicarbonate from the filters is very wet the partial vapor pressure of water in the dryer may become very high, and that the product $P_{CO_2} \times P_{H_2O}$ may then be nearly equal to the equilibrium value, in which case the rate of decomposition

* "Chemical Principles" by A. A. Noyes and M. S. Sherrill, p. 166. The Macmillan Company, New York.

(of calcination) would be very low unless the dryer shell is subject to a much higher temperature. This is why it is essential to keep the moisture content of the bicarbonate as low as possible, to facilitate the dryer operation and not "punish" the shell, to say nothing of the excessive fuel consumption in the dryers.

The heat required to decompose 2 mols of $NaHCO_3$, giving 1 mol Na_2CO_3, 1 mol CO_2 and 1 mol water vapor all at room temperature, is:

$$2NaHCO_3(solid) \rightarrow Na_2CO_3(solid) + CO_2(gas) + H_2O(gas) + Q$$
$$(-2 \times 227,700) \qquad (-272,600) \qquad (-94,400) \quad (-57,800)$$

$$Q = -30,600 \text{ Cal.}$$
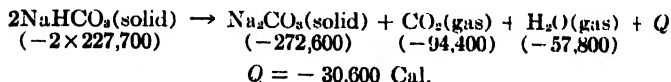
To estimate roughly the theoretical consumption of the coal required per 1000 kg. of the bicarbonate from the filter, given the following data:

Filter bicarbonate at 53% yield
Free moisture in bicarbonate 14%
NH_4HCO_3 in bicarbonate 3.5%
Room temperature .... 25° C.
Temperature, ash extract .... 180° C.
Temperature, flue gases .... 380° C.
Temperature, gases from dryer .... 200° C.
Coal, bituminous slack .... 7,000 kg. Cal. per kg.
Heat of decomposition of $NaHCO_3$ to CO_2 and
  H_2O (gas) .... 30,600 kg. Cal. per kg. mol
Sp. ht. flue gases 0.24
Sp. ht. soda ash .... 0.256 *
Sp. ht. CO_2 gas 0.21
Sp. ht. steam 0.47
Latent heat of evaporation of water at 25° C. to
  steam at 25° C. .... 582 kg. Cal.
Radiation loss from furnace assumed at 25 per
  cent of total heat supplied.
Flue gases from combustion at 80 per cent excess
  air (including water vapor) .... 15 kg. per kg. of coal †

Per 1000 kg. of wet bicarbonate neglecting the small quantities of NaCl, etc., let X = kg. coal per 1000 kg. of the crude bicarbonate:

(1) Heat of decomposition of $NaHCO_3$ to gaseous H_2O and
  CO_2 at 53 per cent yield

$$530 \times \frac{30,600}{106} \quad .... \quad 153,000 \text{ kg. Cal.}$$

(2) Heat of decomposition of NH_4HCO_3 at 35 kg. per 1000
  kg. bicarbonate
$$NH_4HCO_3(solid) = NH_3(gas)$$
$$(-208,600) \qquad (-12,000)$$
$$+ CO_2(gas) + H_2O(gas) + Q$$
$$(-94,400) \quad (-58,000)$$

$$Q = -44,200 \text{ kg. Cal. per kg. mol}$$

$$\frac{35}{79} \times -44,200 \quad .... \quad 19,600 \text{ kg. Cal.}$$

* "International Critical Tables," Vol. V, p. 100.

$$† W = \frac{11 CO_2 + 8 O_2 + 7(CO + N_2)}{3(CO_2 + CO)} \times C$$

  Where W = weight in kg. of flue gases per kg. of coal on dry basis
  C = fraction of carbon in coal
  CO_2 = % CO_2 by volume in flue gases
  CO = " CO " " " " "
  N_2 = " N_2 " " " " "

(3) Heat to evaporate free moisture, 14 per cent (to gaseous
H_2O at 25° C.)
140 × 582 kg. Cal................................. 81,500 kg. Cal.

(4) Heat in the ash extract
530 × 0.256 × (180° − 25° C.) .... 21,000 kg. Cal.

(5) Heat carried away by water vapor at 200° C. in outlet
gases
$$\frac{(14+9)}{100} \times 1000 \times .47 \times (200° - 25° \text{C.})$$ .... 18,900 kg. Cal.

(6) Heat carried away by CO_2 in outlet gases
$$\frac{22}{100} \times 1000 \times 0.21 \times (200° - 25° \text{C.})$$ .... 8,100 kg. Cal.

Total .... 302,100 kg. Cal.

(1) Heat per X kg. coal .... 7,000X kg. Cal.
Less (2) Radiation losses, etc., 25 per cent ....'............... 1,750X kg. Cal.⎫
Less (3) Heat carried to the stack   ⎬
15X × 0.24 × (380° − 25° C.) .... 1,280X kg. Cal.⎭

Net .... 3,970X kg. Cal.

∴ 3970X = 302,100, X = 76.0 kg. of coal per 1000 kg. bicarbonate
∴ the fuel ratio is 76.0 kg. to 530 kg. soda ash obtained or 1:6.9

That is, 0.15 ton of coal is required per ton of ash calcined. The fuel consumption, however, depends also upon the quality of coal burned, the method of firing (hand firing, stoker firing or pulverized coal firing), the construction of the furnace (brick-setting and the construction of flue passages), and the manner and the rate of operation. The above calculation is a very rough one, one biggest factor being the unknown radiation losses from the furnace, which are assumed to be 25 per cent.

In practice, the fuel consumption is 20-25 per cent per ton of soda ash calcined, depending upon the dryness of the bicarbonate and the quality of coal used. The efficiency is therefore even lower. One American manufacturer in the South has been successful in performing this operation with a high-pressure, steam-heated equipment and obtains a higher overall efficiency in this operation (*i.e.*, in the combination of steam boiler and rotary calciner).

The foregoing is a description of the decomposition of sodium bicarbonate into normal carbonate by calcination. Very recently alkali manufacturers in the United States are installing so-called "decomposers" for converting the crude sodium bicarbonate (ammonia soda) directly to the carbonate in solution, furnishing soda solutions for the manufacture of both caustic and bicarbonate of soda. This we have called "Wet Calcination" (see Chapter XXI).

Chapter XIV

Recovery of Ammonia—Efficiency of Operation in Ammonia Still

The price of soda ash is normally about $30 per ton but that of ammonium sulfate $30 to $40.* Based on a 25 per cent ammonia content, the price of ammonia is $120 to $160 per ton, or about 4 to 5 times that of soda ash. Evidently we cannot afford to lose much ammonia in the manufacture of soda ash. Ammonia is a comparatively expensive commodity. One of the reasons for the failure of the ammonia soda process earlier in the history was the lack of an efficient method of recovering ammonia from the mother liquor and the inability to minimize ammonia losses during operation. The heavy losses of ammonia in the cycle made it impossible for the process to compete with the LeBlanc process. It is now a systematic practice in ammonia soda plants to save all ammonia-bearing liquors and send them to the distiller for recovering NH_3. So much attention is now devoted to saving ammonia that it has become almost a matter of habit on the part of plant operators to consider the loss of sodium chloride as a very minor matter in comparison with that of ammonia.

Naturally in the early history of the ammonia soda process the loss of ammonia was great. Toward 1880, the loss of ammonia was still in the neighborhood of 4 to 8 per cent as $(NH_4)_2SO_4$ on the weight of soda ash made. Now the conservation of ammonia in the soda ash plants has received so much attention that the loss is only from 0.20 to 0.40 per cent as $(NH_4)_2SO_4$ on the soda ash produced.

The draw liquor contains from 65 to 74 titer of fixed ammonia and 22-26 titer of free ammonia. In other words, there are approximately a little less than 3 parts of fixed ammonia to 1 part of free ammonia. But the proportion of free ammonia to fixed ammonia in the feed liquor is increased by (1) the addition of the furnace condenser condensate which contains high ammonia and ammonium carbonate; (2) the absorption of free ammonia when a portion of the filter liquor is employed in scrubbing furnace gases (in the furnace gas scrubber); (3) the addition of crude liquor which contains only the free ammonia (but little fixed ammonia) to replace the ammonia lost in the system; and (4) the addition of sodium sulfide solution to make up for the deficiency of sulfide in

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* At present, the price of ammonia because of the production by the direct synthesis is rather low, but the demand and supply will adjust themselves as times get normal.

the ammoniated brine system. The sodium sulfide converts an equivalent quantity of fixed ammonia to "free ammonia."

$$Na_2S + 2NH_4Cl \rightarrow 2NaCl + (NH_4)_2S$$
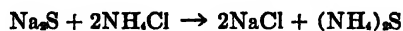
On the other hand, if crude liquor is not available, ammonium sulfate solution is generally made from ammonium sulfate crystals and added to the filter liquor for distillation. This then would increase the ratio of fixed ammonia to free ammonia in the feed liquor to the distiller. On the whole, however, the proportion of free ammonia to fixed ammonia is considerably increased as the filter liquor arrives at the distiller, and the distiller feed may have the ratio of free ammonia to fixed ammonia as high as 3 to 7. At the same time, the liquor on its way to the distiller is diluted, as far as Cl⁻ is concerned, by: ,

  (1) wash water on the filters;
  (2) steam condensate from the furnace condenser drain line;
  (3) steam condensate from gases in the furnace gas scrubber;
  (4) water contained in the crude liquor, or in the ammonium sulfate solution, added to replace the ammonia lost.
  (5) water contained in the sodium sulfide solution added when the sulfide in the crude liquor is insufficient.

The filter liquor is pumped up to feed the distiller through an orifice regulation.

The composition of one sample of crude ammonia liquor is given in Table 92.

TABLE 92. Composition of Crude Ammonia Liquor.

Sp. gr. at 23° C.	1.025
Total ammonia (as NH_3)	20.14%
$(NH_4)_2CO_3$	31.60%
Sulfide as $(NH_4)_2S$	10.98%
NH_3 (free)	3.46%

There are two types of modern ammonia column stills or distillers, one of the internal overflow type and the other of the external overflow type, both consisting of a number of compartments or rings with mushrooms, division plates, and overflow pipes. These rings are placed one above another like a sort of column or tower (Fig. 58). The internal overflow type has a pipe inside each division plate, and the upper end of the pipe controls the depth of liquor or barbotage on the division plate, while the lower end dips well below the surface of the liquor in the next compartment below to give the necessary seal. These overflow pipes alternate from one division plate to another in a diametrically opposite position, so that the liquor is obliged to travel across each plate and down in a zigzag manner (Fig. 59).

The external overflow type has these overflow connections outside of the distiller from one ring to the next below, alternating in diametrically opposite positions as above. The edge of the overflow opening in this case controls the height of the liquor in each section and the inlet opening

into the section below is located well below the level of the liquor line. These overflow pipes are usually rectangular in cross-section, long horizontally and narrow vertically; and in order to provide the most direct flow for the lime sludge which has a great tendency to plug the passage, the horizontal part of the shoulder connecting the overflow pipe with the side of the distiller is made as short as possible. In fact, one construction has the overflow trough directly attached to the side of the distiller, making the outside wall of the distiller the bottom side of the rectangular overflow trough.
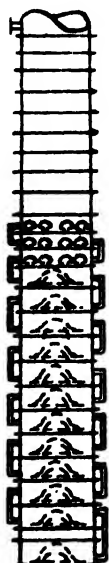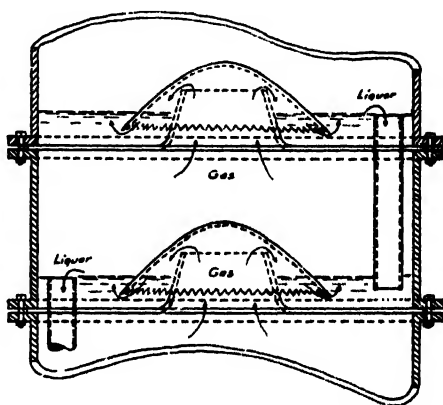
FIG. 59. Distiller sections of internal overflow type.

FIG. 58. Distiller.

The advantages of the internal overflow type are a more direct passage for the thick lime sludge to travel from one section to another below, and no heat losses by radiation from these overflow conduits. The advantages of the external overflow type, on the other hand, are that a clear space inside the distiller is available for ammonia distillation and that the overflow passages are more accessible. At present the external overflow type is common in soda plants (Fig. 60).

The size of the mushroom in each compartment is dependent on the shape of its sides or wings. The diameter of the mushroom at the base of its serrated edge is generally from 55 to 70 per cent of the inside diameter of the compartment. For example, for a 2500-mm inside diameter, the diameter of the mushroom may be from 1400 to 1700 mm. For a mushroom with a steep slope at the sides, of the type shown in Fig. 59, the diameter should be smaller; while for a mushroom with widespread sides of the type shown in Fig. 61, this diameter takes a somewhat higher ratio. Often the bottom of the compartment (the division plate) is

curved in the manner shown in Fig. 60, the idea being so to direct the flow
of steam that it may come into intimate contact with the whole volume
of the liquor and may spread itself in fine bubbles in the liquor, encoun-
tering least resistance in its radial sweep. With a large number of mush-
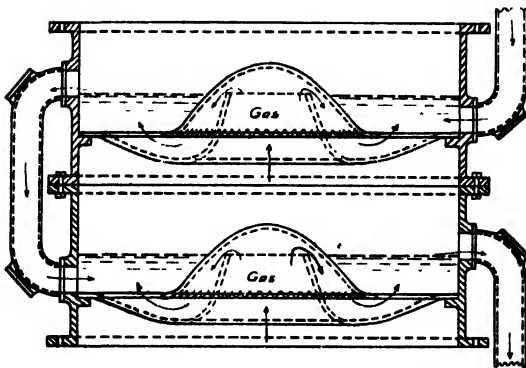
Fig. 60. Distiller sections of external overflow type.

rooms placed one on top of another throughout the height of the distiller,
the resistance may be considerable, especially if the depth of the liquor
in each compartment (the depth of wash or barbotage) is considerable.
For ammonia absorption, such as in an absorber where the gas is to be
dissolved by the brine, the depth of the wash should be greater; but for a
distilling operation as in the distiller discussed here, the quantity of the
liquor carried in each compartment should be small.
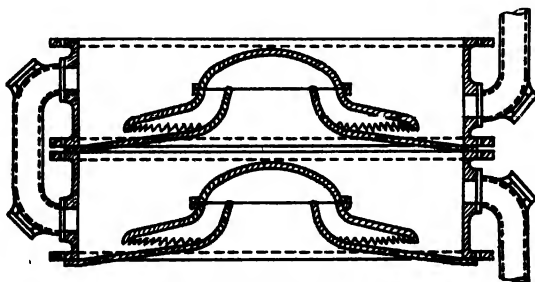
Fig. 61. "Bubble-Cap" type of heater sections.

If the diameter of the compartment is large, a multiple system of
mushrooms is provided to distribute the steam evenly over the entire
area of the compartment; in this case, either several long, narrow mush-
rooms or several small, circular mushrooms are placed at equidistant
points on the division plate.

One important point that should be observed in the design of the dis-
tiller is so to proportion the mushroom dimensions and so to locate the
overflow points that the liquor shall have no tendency to be blocked up
by the upward flow of steam. A condition in which the upper compart-

ments tend to run full and the liquor refuses to descend readily is known as the "suspension" of the liquor (similar to the "gas-locking" or "gas-binding" in the absorber). Normally, this is caused by the deposit of scale or sludge at the overflow points; but with faulty design of the bubble-caps and division plates, this tendency is greatly increased, with the result that steam enters the liquor passage and blocks its downward flow.

A column distiller for soda manufacture consists of three main parts: the upper part above the lime inlet, called the "heater"; the lower part below the lime inlet, the lime still, or the distiller proper; and the partial condenser located on the top of the heater. The heater is to vaporize "free ammonia" from the filter liquor by steam, and the lime still is to decompose the fixed ammonia by milk of lime and vaporize the free ammonia so liberated by steam. The partial condenser is to provide the overflow to the top of the heater and to secure richer (drier) ammonia gases distilled over. Under "free ammonia" are included (besides free NH_3), NH_4HCO_3, $(NH_4)_2CO_3$, $(NH_4)_2S$, etc., i.e., all the ammonium compounds that are readily decomposable and volatilized by steam. The fixed ammonia which requires lime is mostly in the form of NH_4Cl, and in small quantities also in the form of $(NH_4)_2SO_4$. This column type of distiller was the invention of Dr. Ludwig Mond, who designed and built it in 1883.

The older forms of lime still consisted of four large tanks in series. Steam entered the one containing the weakest ammonia liquor, and the outlet from this went to the next, and so forth. When all the ammonia in one unit had been boiled out, it was cut out and the content emptied. Steam entered the next one in the series as a head tank. The empty kettle was filled with filter liquor and the requisite quantity of milk of lime, and became the last one in the series. This is a batch process. The handling required considerable labor. Although there might be a saving in lime by being able to control the quantity of lime in each batch, the time and labor involved made it unsuitable for any large-scale production.

The reactions in the heater are as follows:

(1) $NH_3 . Aq \rightarrow NH_3$ gas
(2) $NH_4HCO_3 \rightarrow NH_3 + H_2O + CO_2$
(3) $(NH_4)_2CO_3 \rightarrow 2NH_3 + H_2O + CO_2$
(4) $NaHCO_3 + NH_4Cl \rightarrow NaCl + NH_4 + H_2O + CO_2$
(5) $Na_2CO_3 + 2NH_4Cl \rightarrow 2NaCl + 2NH_3 + H_2O + CO_2$
(6) $(NH_4)_2S \rightarrow 2NH_3 + H_2S$
(7) $NH_4HS \rightarrow NH_3 + H_2S$
(8) $Na_2S + 2NH_4Cl \rightarrow 2NaCl + 2NH_3 + H_2S$
(9) $Na_2S + CO_2 + H_2O \rightarrow Na_2CO_3 + H_2S$

The reactions in the lime still or distiller proper are:

(10) $Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$
(11) $CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$
(12) $2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O$
(13) $(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2NH_3 + 2H_2O$

The following reaction:

(14)　$CaCO_3 + 2NH_4Cl$ (or $(NH_4)_2SO_4$)　　　$CaCl_2$ (or $CaSO_4$) $+ 2NH_3 + CO_2 + H_2O$

requires prolonged cooking over a long period to get satisfactory completion. It takes place only when finely divided calcium carbonate, such as the precipitated carbonate from the causticization tanks, is used in excess and also when the ammonium chloride concentration is high. Under the prevailing conditions of distiller operation, however, such a reaction does not occur to any extent. For the same reasons, with the insoluble magnesium oxide in milk of lime, the reaction

(15)　$MgO + 2NH_4Cl \rightarrow MgCl_2 + 2NH_3 + H_2O$
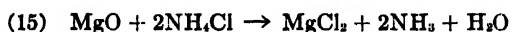
can hardly take place in the lime still under ordinary conditions.

The heater is either packed with coke, about 6 inches in size, or with earthenware tiles, the so-called chemical tiles. The spiral tiles made of stoneware are best of 5 inches inside diameter by 6 inches outside diam-
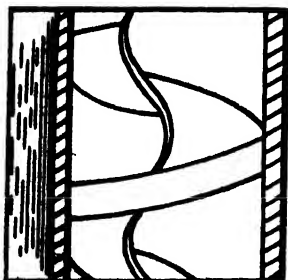
FIG. 62. Spiral chemical tile.　　FIG. 63. "Spray dish" type of heater sections.
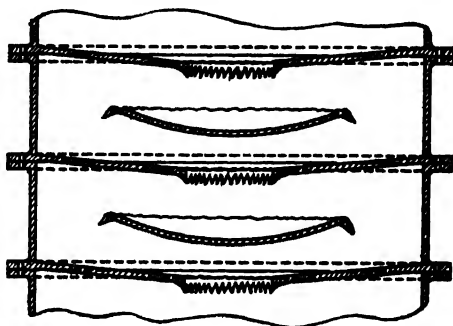
eter and 6 inches high, with a spiral ribbon inside (Fig. 62). Some heaters also have mushrooms and division plates (the "bubble-cap" type) as in the distiller proper (Fig. 61), while others have, instead of these, inverted spray dishes having serrated edges with serrated overflow openings in the center of the division plates underneath (Fig. 63). Still others have sections consisting of long, narrow mushrooms on each division plate (as in Fig. 38, p. 170). A good distribution method is to use a large number of long and narrow distributing troughs or trays, packed one on top of the other and staggered over each other, in the manner of the packing in some of the deaerating heaters for the liberation of oxygen from boiler feedwater (see Fig. 64). But in a large majority of cases a combination of these "bubble" or "spray" devices and the tile or coke packing is used. Coke packing offers more resistance to the gas passage than tile packing and may build up excessive pressure. The coke-packed heaters while working properly when properly packed, are likely to become partially plugged by dirt. When this happens, steam blows to one side and chan-

nelling occurs, when a portion of the coke may be blown up forming a pit on the top of the packing. The distiller proper (the lime still), on the other hand, always has the simple mushrooms and the division plates (or bubble-caps and plates).

On top of the heater are sections of the coolers and condensers, usually consisting of a large number of horizontal 2-inch cast iron tubes (Fig. 65). These are divided into two main divisions, the upper division of which uses water as the cooling medium, while the lower division uses the filter liquor as the cooling medium so that the feed liquor is preheated on its way to the heater. These are partial condensers for the ammonia gases,
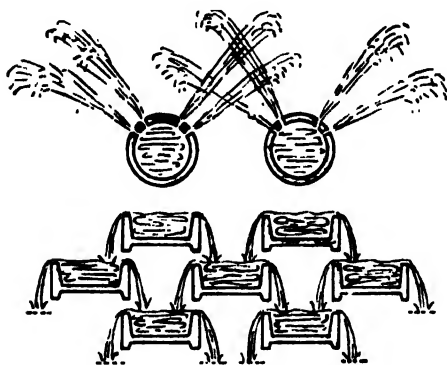
FIG. 64. Distributing trays.
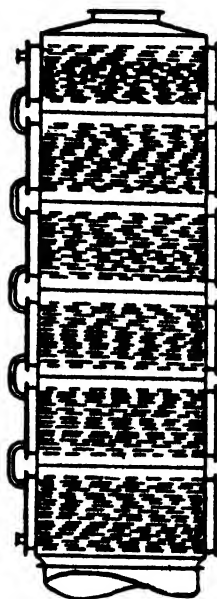
FIG. 65.
Distiller condenser.

and the condensate is allowed to drain back to the heater. The feed liquor is thus heated to about 70° C. before entering the heater. The gases from the distiller consist of ammonia, carbon dioxide, steam, and some hydrogen sulfide and air. The steam, of course, should be condensed out as far as possible, but with it also a portion of the ammonia vapor. Hence the condensate returned to the distiller is necessarily a strong ammonia solution carrying some CO_2. The purpose of the distiller coolers and condensers is to condense out most of the steam, thereby obtaining a sufficiently dry ammonia gas for the absorber operation. Hence the top portion of the distiller, including the coolers and condensers and a part of the heater, may be called a rectifier or dephlegmator. As was explained in detail in Chapter VII, excessive steam carried over by the ammonia gas from the distiller would unnecessarily dilute the brine and generate too

much heat in the absorber. Sometimes the distiller coolers and condensers are installed separately and located below the distiller top, but their proper place is on the top of the distiller so that the condensate may be drained back directly to the heater where the strong ammonia liquor properly belongs. When they are installed separately, they are placed high enough so that the condensate may flow into the heater through a U-loop seal. This is done to avoid pumping the hot, corrosive ammonia-carbon dioxide condensate back to the top of the distiller. The distiller coolers and condensers are subject to very severe chemical corrosion because of the presence of ammonia, CO_2, H_2S, etc., carried by the ammonia gases at an elevated temperature. The cooling tubes must be made of a good grade of cast iron (not steel) to withstand the corrosion.

Liquor from the bottom of the heater, which should be free from CO_2, flows to the top of the lime still or the prelimer, where milk of lime is introduced to decompose the fixed ammonia; and the free ammonia so liberated is distilled off by steam just as in the heater above, as the liquor flows down from one passette to another in the lime still. In actual operation, in the arrangement in which the heater is placed on top of the lime still, not all the free ammonia can be driven from the heater liquor. On arriving at the bottom of the lime still, however, all ammonia should have been distilled out, leaving the waste liquor with a small excess of lime to be run off to waste. Open steam enters at the bottom compartment in the lime still diametrically opposite the blow-off opening. In actual practice, exhaust steam from the engines, or better from the bleeder turbines, is employed for this purpose. The engine cylinders are so designed as to give 8 to 10 pounds back pressure in the exhaust. Generally, there is a tendency toward shortage, rather than surplus, of the exhaust steam for distillation, and at times some live steam may have to be introduced into the distiller. Live steam is not so suitable as the exhaust steam which, by virtue of its low pressure, has a large volume, giving a large contact surface and more even bubbling action in the distiller. The exhaust steam, however, must be dry and the condensate trapped out in order to avoid unnecessary dilution in the distiller.

The rate of decomposition of the fixed ammonia by lime is wholly dependent upon the rate of hydration and solution of CaO in the lime still. While the ionic reaction is instantaneous, the solution of CaO is slow; which, therefore, controls the speed of its reaction with fixed ammonia.

$$CaO \text{ solid} \rightleftharpoons CaO \text{ diss.} \rightleftharpoons Ca^{++} + 2OH^-$$
$$Ca^{++} + 2OH^- + 2NH_4^+ \rightarrow Ca^{++} + 2NH_4OH$$
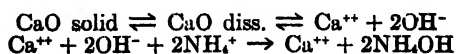
Lime has the peculiar property of becoming less readily soluble when burned at a high temperature, *i.e.*, when it is overburned or dead-burned it dissolves with great difficulty. In order to make more lime available for ammonia liberation, the time of contact in the liquor should be lengthened. This is accomplished by having a large reservoir outside where the heater liquor is intimately mixed with the milk of lime and

allowed much longer time of contact before entering the lime still. This reservoir, called the prelimer or preliming tank, is provided with a stirrer to keep the milk of lime in suspension, and the heater liquor in intimate contact. By gradual displacement, the top portion of the liquor overflows to the lime still. Thus, a major part of the reaction is caused to take place in the prelimer outside, returning virtually free ammonia liquor to the lime still for distillation. There are several advantages in having the prelimer. First, it gives a more thorough mixing of milk of lime and heater liquor; secondly, it allows more time for lime to dissolve and react with the fixed ammonia; and thirdly, it affords easier control of the excess of lime in the distiller, avoiding sharp fluctuation in the lime used for distillation.

The volume of filter liquor by the time it reaches the distiller is about 7 cubic meters per ton of ash. Table 93 gives its approximate composition after the liquor has received various ammonia condensates and liquors.

TABLE 93. Composition of Distiller Feed Liquor.

Fixed NH_3	55 titer
Free NH_3	25 titer
NaCl	75 grams per liter
CO_2	35 grams per liter

The heater liquor contains all the fixed ammonia and sodium chloride, and should contain no CO_2 or free ammonia. But in practice, as mentioned above, there still remains about 4 titer of free NH_3. The freedom from CO_2 in the heater liquor is a test for the efficiency of the heater, and is generally dependent upon (1) the temperature in the heater, (2) the intimate and thorough contact between the liquor and the steam in the heater, and (3) the time that the liquor is exposed to the action of steam, assuming a uniform gradient of the partial vapor pressure of ammonia throughout the heater. The heater liquor should be practically free from CO_2 before entering the prelimer, or the calcium hydroxide would be converted to calcium carbonate, which is unavailable for ammonia liberation in the lime still. For the following reaction, as mentioned above,

$$CaCO_3 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3 + CO_2 + H_2O$$

does not take place under normal operating conditions in the lime still.

The pressure at the bottom of the distiller should be from 8 to 10 lbs. gage (sometimes as high as 12 lbs.); and there should be a slight vacuum at the top of the distiller, about $\frac{1}{4}$ inch Hg, so that the pressure in the distiller decreases from 8 to 10 lbs. per sq. in. at the bottom to a slight vacuum at the gas outlet at the top. The use of a slight vacuum at the top decidedly helps the vaporization of ammonia in the liquor. The whole distiller and absorber system must be air-tight; or air will leak in and render the exhaust gas from the absorber system too weak in CO_2 to be returned to the carbonating towers. In any case a slight vacuum is to be preferred both from the viewpoint of avoiding loss of ammonia gas to the

atmosphere and of the more rapid removal of ammonia vapors from the distiller. The top temperature is 82 to 86° C.

Roughly speaking, as described above, the heater and the condenser may be said to correspond to a rectifier and the lime still to the distiller proper. However, as it is actually conducted in ammonia soda plants, the function of each portion of the distiller is not so simple. When the heater is set on top of the lime still integrally, the rich ammonia gas from the lime still below is not (and cannot be) in equilibrium with the liquor in the heater. The heater then cannot be purely a rectifier or dephlegmator, because while receiving the overflow at the top from the partial condenser, it also receives dilute feed liquor. Its function is primarily to distill "free ammonia" from the feed liquor, and consequently cannot be simply one of rectifying or dephlegmation. Again, the heater liquor containing fixed ammonia is limed in an outside tank (preliming tank or prelimer) and then returned to the top of the lime still, containing some excess lime. This is really another feed to the distiller introduced at another point of the distiller body. Hence the whole distiller is in reality a two-feed column (filter liquor at the top of the heater and a limed liquor at the top of the lime still coming from the prelimer), entailing complexities inherent to a two-feed system—nevertheless a simple two-component (ammonia-water) system where the composition in the vapor phase from the top of the lime still is not in equilibrium with that in the liquid phase from the bottom of the heater, and where the rich ammonia gas from the top of the heater is not in equilibrium with the rather cold, dilute filter liquor introduced there.

As the bottom of the distiller is under a pressure of 8-10 lbs. gage, the liquor is therefore at a temperature above the boiling point under atmospheric pressure. When, therefore, the liquor is blown out and is released to the atmospheric pressure, it partially flashes into steam, which can be utilized for distillation at a lower pressure. Indeed, in practice, the blow-off is first blown into a flash tank near the bottom of the distiller and the steam from the uptake of the flash tank is utilized to operate a weak liquor distiller which is merely a small still about 1 m. in diameter and 8 m. high, distilling floor liquor and other weak ammonia liquors. Such a weak liquor distiller has been installed in most ammonia soda plants, utilizing the blow-off steam.

TABLE 94. Composition of Distiller Scale.

	Per Cent		Per Cent
$CaSO_4$	62.41	NaCl	1.65
CaO	30.32	Fe_2O_3	0.20
$MgSO_4$	2.35	Al_2O_3	0.08
$MgCO_3$	1.62	SiO_2	0.32
Na_2SO_4	1.17	Moisture	0.60

In the lime still or the distiller proper, hard scale is likely to form and the distiller needs to be shut down and cleaned every so often. This happens once in 1 or 2 months, depending upon the rate of operation and

the quality of lime used. Frequent interruption in the distiller operation would cause solids to settle in the lime still, necessitating more frequent cleaning. The scale formed in the upper portion of the lime still contains much calcium carbonate; while calcium sulfate predominates below, although lime is also present in considerable quantities.

Table 94 gives the results of analysis of a scale taken near the bottom of the distiller.
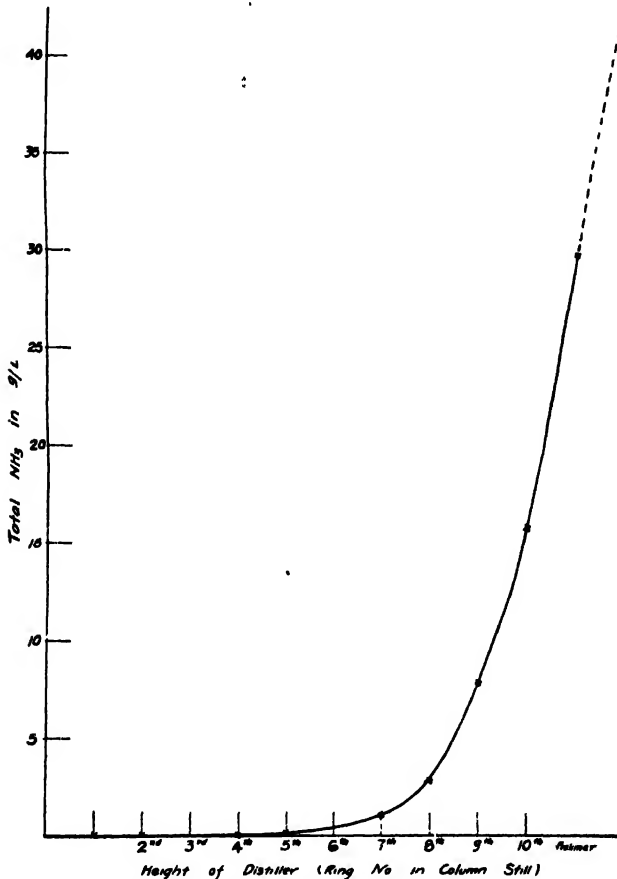
Fig. 66. Analyses of distiller liquor showing condition of operation.

This scale is very hard and attains a thickness of 1 to 2 inches. It has to be chiselled off by hand or by a pneumatic scaling hammer. Before shutting down a distiller, it should be cooked for several hours with steam to drive out all ammonia. The distiller is then cut out and allowed to cool. The manhole covers are opened and the cleaning work is started.

Table 95 gives some idea about the ammonia concentrations in the different samples at different points in a distiller in operation. Figure 66

shows the ammonia gradient in the liquor phase in the lime still and the prelimer.

TABLE 95. Analyses of Distiller Liquors Showing Condition of Operation.

	Sample	Sp. Gr. and Temp.	Total NH_3	Total Chlorine (as Cl^-)
			Grams per Liter	
	Filter liquor	1.122 at 27° C.	61.20	140.82
	Heater liquor	1.093 at 27° C.	43.03	125.55
Heater and prelimer	Prelimer liquor	1.120 at 26° C.	29.89	99.26
	Ring No.			
	10	1.121 at 23° C.	15.78	90.56
	9		7.93	
	8		2.83	
	7		1.04	
Lime still	6	,	....	
	5		0.108	
	4		0.025	
	3		....	
	2		0.018	
	1		0.012	

As to the composition of the liquors in different rings of the distiller, Bradburn's * data in Table 96 illustrate the conditions of operation in the distiller at his time.

TABLE 96. Composition of Liquors at Different Points in Distiller.

		Total NH_3	Free NH_3	Fixed NH_3	CO_2
			Grams per Liter		
	Feed liquor	67.2	15.0	52.2	39.3
	Ring No.				
	21	83.4	39.0	44.4	26.2
	20	74.0	30.7	43.3	9.0
	19	66.0	23.1	42.9	3.8
	18	62.8	20.4	42.4	2.0
Heater	17	60.5	18.5	42.0	1.2
	16	57.7	16.2	41.5	0.71
	15	55.0	13.8	41.2	0.38
	14	53.0	12.1	40.9	0.20
	13	52.6	12.1	40.5	nil
	12	39.0	39.0	nil	nil
	11	9.7	9.7	nil	nil
	10	4.0	4.0	nil	nil
	9	1.9	1.9	nil	nil
	8	1.0	1.0	nil	nil
	7	0.6	0.6	nil	nil
Lime still	6	0.33	0.33	nil	nil
	5	0.20	0.20	nil	nil
	4	0.13	0.13	nil	nil
	3	0.05	0.05	nil	nil
	2	0.03	0.03	nil	nil
	1	0.017	0.017	nil	nil

The distiller waste, or run-off liquor, contains all the undecomposed salt in the filter liquor, calcium chloride in a quantity equivalent to the

* Ullmann, "Enzyklopädie der technischen Chemie," Vol. 8, p. 31, Berlin, Urban & Schwarzenberg, 1931.

amount of sodium chloride decomposed, a small quantity of calcium hydroxide (2 to 4 grams per liter) from the slight excess of lime used to insure the complete decomposition of fixed ammonia in the lime still, and all the impurities of sand, unburned and overburned stone, etc. present in the lime. The composition of the waste liquor varies greatly according to the quality of brine and limestone used, the volume of the feed liquor to be distilled per ton of ash, the percentage of decomposition in the towers, and the strength of the milk of lime employed. Normally, there are about 10 to 12 cubic meters of the waste liquor per ton of ash made. (See Table 97.)

TABLE 97. Calculation of Volume of Distiller Waste.

	For Small Works Where Dilution is Comparatively Great	For Average Conditions
	Cubic Meters	
Draw liquor	6	5.4
Wash water on the filters, steam condensate, condenser drain, etc.	1	0.6
Milk of lime	2½	2.0
Dilution by exhaust steam	2½	2.0
Total	12	10.0

The composition of the distiller waste also varies greatly. Its approximate composition is shown in Table 98.

TABLE 98. Composition of Distiller Waste.

Sp. gr. of waste liquor	1.10-1.13
CaCl₂	85-95 grams per liter
NaCl	45-50 grams per liter
CaCO₃	6-15 grams per liter
CaSO₄	3-5 grams per liter
Mg(OH)₂	3-10 grams per liter
CaO	2-4 grams per liter
Fe₂O₃ and Al₂O₃	1-3 grams per liter
SiO₂	1-4 grams per liter
NH₃	0.006-0.012 gram per liter

The composition of the distiller waste liquor and the relative concentrations of various substances therein is a barometer indicating the efficiency of the whole ammonia soda process. For, from the analysis of this liquor, it is possible to obtain many data bearing on the consumption of raw materials employed and consequently the efficiency of the operation. For instance,

(1) Low specific gravity of the liquor and the proportionately low concentrations of various substances present indicate a large volume of feed liquor to be distilled and consequently a high consumption of steam and coal, and a greater ammonia loss per ton of ash.

(2) Low ratio of calcium chloride to sodium chloride indicates low decomposition in the carbonating towers (or columns) and high wastage of sodium chloride.

(3) Presence of much ammonia indicates a heavy loss of ammonia through the distiller.

(4) High percentage of lime indicates a large excess of milk of lime and high consumption of limestone.

(5) High percentage of calcium carbonate indicates inefficient operation in the heater (from CO_2 in the heater liquor) and high consumption of lime and coke.

(6) Large amounts of insoluble solids in the waste liquor relative to calcium chloride, such as magnesium oxide, silicon dioxide, ferric oxide, and aluminum oxide (all of which must have come from the milk of lime), indicates poor quality of limestone being used.

The distiller waste liquor carries considerable solids in suspension. The disposal of this waste is a matter of no little concern to ammonia soda manufacturers. The solids accumulate very fast, and the liquid portion containing free lime and calcium chloride, if allowed to run into a stream, may kill the fish and contaminate the water. Towns where the industry is located will pass laws forbidding the discharge of this waste to the river in the community. The general practice is to employ a large tract of land, 100 acres or larger, adjoining the factory site and pipe the waste in 8- to 12-inch steel pipes first to one-half of this field and then to the other. Settling takes place and the solids are left behind. Only the liquid portion is allowed to flow out. How fast these solids accumulate can be appreciated from the fact that one plant producing 100 to 150 tons of ash daily filled a piece of land 10 acres in area to a height of 20 feet in about 9 years. As the solids build up in one half of the land, they are dug out and thrown on the sides, making an embankment surrounding it. Meanwhile, the discharge goes to the other half. As the land is being filled up, the elevation becomes too much for the gravity flow of the liquor from the bottom of the distiller. A centrifugal booster pump is then employed to give the head necessary to discharge to these fields. If limestone quarries lie near at hand, the waste is best sent to fill the old quarry pits.

The waste as shown above contains chiefly calcium chloride, sodium chloride, calcium carbonate, silicious matter, and lime. Attempts have been made to work up this waste liquor for anhydrous calcium chloride, refined salt, etc. In fact, several ammonia soda plants are doing this. But the limited demands for calcium chloride in comparison with the quantity produced can utilize hardly a fourth or a fifth of the total output. The balance has to be disposed of.

The blow-off liquor from the bottom of the distiller is at a temperature slightly above the boiling point of plain water. Its sensible heat is therefore enormous because of the very large volume involved. This will later be shown by the fact that it takes about 64 per cent of the total heat required just to heat up the liquor. The heat in the blow-off liquor should therefore be utilized for preheating, but unfortunately the liquor contains considerable suspended solids which may settle and form scale

in a preheater or heat exchanger, making the scheme impracticable. Some heat, however, is utilized in evaporation when the clarified blow-off liquor is evaporated for the recovery of calcium chloride and salt.

The distiller operation is rather delicate in its control, and good judgment must be exercised at all times. The rate of feed, the varying composition and concentrations of the feed liquor, the adjustment of the quantity of milk of lime to give the proper excess, the varying strength in the milk of lime—all demand close attention on the part of the operators. If there is a deficiency of steam, ammonia may not be completely driven out before the liquor reaches the bottom. This is a phenomenon called the "Sour Bottom," in which case the sour liquor at the distiller bottom must be temporarily emptied out to a pit to be pumped back to the distiller later; otherwise much ammonia would be lost in the waste. Also in such cases CO_2 may not be completely driven out from the heater liquor, and the sulfide from sodium sulfide added may not be completely decomposed: some may remain in the distiller waste and be lost. If, on the other hand, too much steam is used, it may be beyond the capacity of the condensers and coolers to cool, the gas outlet temperature would be too high, and the gas would carry over too much steam to the absorber. Normally the gas enters the absorber at a temperature of 55 to 60° C. A temperature much lower than 55° C. may, if allowed to remain for any length of time, cause crystallization of "ammonium carbonates" both in the distiller cooler passage and in the gas mains leading to the bottom of the absorber, thereby plugging up the system. On the other hand, a temperature above 60° C. would bring too much steam condensate to the absorber, unnecessarily diluting the brine, with the result that the Cl^- titer in the ammoniated brine falls low. This, of course, causes low decomposition in the columns because of low concentration of Na^+ in the green liquor. A serious case that sometimes ensues is the "hot-top" condition in the absorber created by the heat thus carried to the absorber from the condensation of much steam.

Further, if there is a deficiency in lime, there will be some undecomposed fixed ammonia at the distiller bottom. The liquor, of course, would then smell "sweet," but ammonia may have been sent to waste unnoticed. As ammonia is an expensive material and normally the still is the largest single source of ammonia loss, the liquor at the still bottom should be continually titrated for an excess of lime and tested for "sweetness" by its odor as often as every few minutes.

Regarding the corrosion of the apparatus by ammonia, Pennock and Morton * found that if the iron surface was clean and free from rust, ammonia not only would not corrode the iron but would protect it. If, on the other hand, corrosion of iron had started, ammonia would accelerate it. It is therefore necessary to have a ferrous sulfide coating on the exposed surface of the iron to prevent corrosive action.

* *J. Am. Chem. Soc.,* p. 377 (1902).

EFFICIENCY OF AMMONIA STILL OPERATION

The distillation of ammonia from the filter liquor is an example of separating a more volatile constituent from a less volatile one, when the two are soluble in each other in practically all proportions, to form one liquid phase. It is a binary solution with one liquid and one gaseous phase. The system is therefore divariant. The fixing of any two factors, or independent variables, out of the three—temperature, pressure, and composition in the liquor—will thus determine the whole system. These are generally the temperature in the still and the composition in the liquor, the two being as far as possible maintained constant or uniform in the distiller operation.

Aqueous ammonia solutions behave quite normally. The ammonia concentration in the vapor phase in equilibrium with the solution is consistently greater than its concentration in the solution at all temperatures and in all concentrations, there being no maximum or minimum constant boiling point for the solution. In a dilute solution its vapor pressure may be said to follow Henry's law.
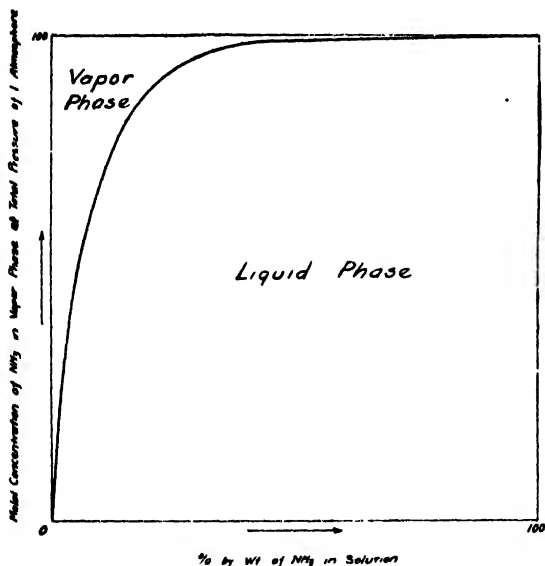
Fig. 67.

Composition of ammonia in vapor and liquid phases.

That is, if c is the concentration of ammonia in solution, and C that in the vapor, $C > c$ at all concentrations in the solution (Fig. 67). The partial vapor pressure of ammonia in equilibrium with dilute solutions at 30° C., within the range of from 0 to 40 grams NH_3 per liter, may be expressed as follows:

$$p = 0.99 \, C$$

where

p = partial vapor pressure of NH_3 in mm Hg
C = conc. of NH_3 grams per 1000 grams of H_2O

As described above, the modern ammonia distiller consists of a lime still and a heater set on top of the lime still, receiving ammonia vapors and all the heat from the lime still below. Although this gives a simple arrangement, it is not done without some sacrifice. For, while a countercurrent arrangement in the heat transfer is thus maintained, this is not true of the ammonia vapor flow, and also frequently is not true of the introduction of the feed liquor.

In order that a distiller may operate efficiently the following conditions must be satisfied:

(1) There shall be a countercurrent heat supply to the distiller.

(2) The distiller body shall be insulated against radiation losses.

(3) The partial pressure of ammonia in the vapor rising from bottom to top shall not at any point be greater than the ammonia vapor tension in the liquor with which the vapor comes in contact.

(4) The feed liquor shall be preheated and introduced at a point where its ammonia vapor tension is greater than the partial pressure of ammonia at that point.

(5) The volume of filter liquor to be distilled and of the milk of lime employed per ton of soda ash shall be as small as possible, *i.e.*, both of these shall be as concentrated and hot as possible.

(1) **Countercurrent heat supply.** Although ammonia gas is readily expelled from the solution, the last trace of it is driven out with considerable difficulty. Hence, as ammonia in the liquor gets dilute, more steam and a higher temperature are required to complete the work with a given excess of lime. The supply of steam is so arranged that the weakest ammonia liquor meets the fresh steam, and is subject to the highest temperature available, before the waste liquor is run out. The supply of exhaust steam in the form of open steam is introduced at the bottom of the lime still and the countercurrent feature is closely adhered to in practice.

(2) **Lagging of distiller body against radiation.** The vapors of ammonia and steam in the distiller rise and gradually meet the stronger overflow liquors from the upper division plates. In equilibrium with the increasing ammonia concentrations in the overflows above, the vapor in contact with the liquors is gradually enriched in ammonia. When the vapor strikes the condensers at the top of the distiller, a large portion of steam with a comparatively small portion of ammonia is condensed and flows back to the still. The distiller condensers on top of the heater form what is known as a partial condenser as mentioned before. In the ideal condition, the vapor from one compartment below should be condensed on the division plates above, giving all its heat of condensation for the vaporization of a richer liquor on that plate, and so on, so that a poorer ammonia vapor disappears and in its place appears a richer one. This process is repeated until the partial condenser on the top is reached. Furthermore, it can be shown that in order to obtain a maximum separation between ammonia and water, the amount of overflow from each divi-

sion plate throughout the body of the distiller should be the largest possible. That means that all condensation by cooling should be done in the partial condenser at the top of the heater, and the overflow should start from this partial condenser down. If there is a loss of heat by radiation from the body of the distiller, the vapor will be condensed in the lower part of the distiller before it reaches the partial condenser at the top, and this condensate gives rise to overflows arising from the lower division plates only. Hence, to utilize all the heat coming in the form of vapor below for vaporizing a richer liquor above, and to secure the maximum overflow possible from the division plates throughout the height of the distiller, it is necessary to insulate the body of the distiller and to minimize the heat loss by radiation, so that all the cooling shall be done in the partial condenser and cooler at the top of the heater, and not in any part of the body of the distiller.

(3) **Larger ammonia tension in liquor phase than partial ammonia pressure in gas phase.** In order to cause ammonia to vaporize from the liquor, its vapor tension in the liquor must be greater than the partial pressure in the vapor. If the partial pressure is greater than that which corresponds to the equilibrium value of the tension in the liquor, ammonia from the vapor will be dissolved in the liquor. At equilibrium, the rate of vaporization of ammonia from the liquor equals that of solution in the liquor. While this countercurrent principle is followed on the whole in actual practice, there are departures at certain points in the distiller, notably at the junction between the heater and the lime still and at the feed inlet at the top of the heater. In the distiller construction prevalent in ammonia soda plants, the heater takes all the heat from the lime still, and all the rich ammonia gas from the lime still below is allowed to come in contact with the heater liquor at the bottom of the heater; which liquor contains practically all the ammonia as fixed ammonia. The ammonia vapor tension from the fixed ammonia liquor is practically nil, and consequently at this point some ammonia from the vapor phase will be redissolved in the liquor until equilibrium takes place. This is why the heater liquor leaving the bottom of the heater cannot be completely free from free ammonia in this type of arrangement. This decreases the efficiency of ammonia separation in the distiller and increases the burden on the lime still. The old arrangement of having a separate heater and lime still taking their heat supply (steam) independently and delivering the ammonia gases to a common condenser, also independently, did not have this objectionable feature.

(4) **Feed liquor introduced at a point where its ammonia tension is not smaller than partial pressure of ammonia in gas at that point.** Another point is the feed inlet at the top of the heater. In order not to break the gradient of ammonia concentrations in the overflow liquors, the feed should be introduced at a point where its ammonia vapor tension is just larger than that of the overflow liquor at that point. At the top of the heater where the filter liquor is customarily introduced, the hot condensate from the partial condenser is usually at a much higher ammonia

vapor tension than that in the feed liquor introduced there, especially when the latter is dilute and comparatively cold; and so the gas is richer in ammonia than that which corresponds to the equilibrium value in the feed liquor. As a result, ammonia vapor is actually redissolved by the feed liquor under such conditions. In the present-day ammonia soda plants effort has been made to preheat the feed liquor by using it as a wash liquor in the furnace gas scrubber and further as a cooling medium in one section of the partial condenser at the top of the heater. This not only conserves the heat by treating the partial condenser as a heat interchanger, but also improves the ammonia tension gradient in the heater. The condition is illustrated qualitatively in Figs. 68, 69, and 70.
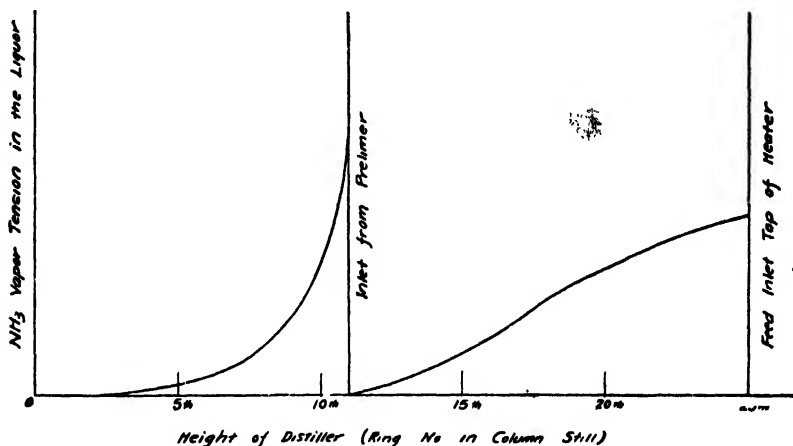
FIG. 68. Curve showing vapor tension of ammonia in liquor phase.

At x_1, Fig. 69, re-solution of ammonia from the vapor always occurs, and at x_2 re-solution of ammonia may occur if the feed liquor is dilute and not properly preheated. Fig. 70 shows the resultant condition from the combination of the conditions in Figs. 69 and 68. The same is particularly true of the mud inlet. The mud from the settling vats, which contains rich free ammonia and CO_2, should enter at the top of the heater.

(5) **Minimum volume of filter liquor to be distilled and of milk of lime used.** From the above it is seen that one objection in the distiller operation is the weak feed liquor, *i.e.*, a large volume of filter liquor to be distilled. In the matter of heat consumption in the distiller, a large volume of filter liquor requires a correspondingly large amount of steam for distillation. This means a wastage of steam and consequently of coal. In the matter of ammonia loss, a large volume of filter liquor means a correspondingly large volume of the waste liquor to be disposed of. As there is always a small amount of ammonia left in the distiller waste liquor, a large volume of this waste liquor would result in a higher ammonia loss through the distiller. Indeed, in normal operation, the distiller is a source of the largest single item of ammonia loss. For the same reason the milk

of lime must be made as strong as can be handled, *i.e.*, containing about 250 grams per liter, or 180 titer lime. For high efficiency it is therefore imperative to keep the volume of filter liquor as small as possible and to employ as strong a milk of lime as can be handled through the pumps
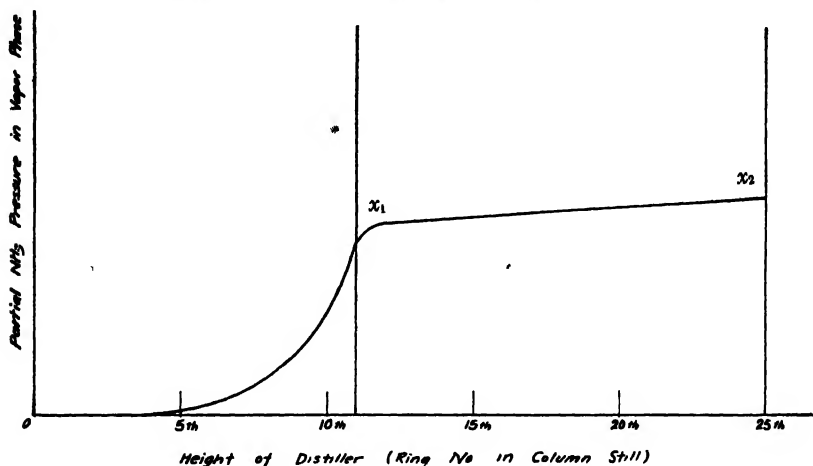
FIG. 69. Curve showing theoretical partial pressure of ammonia in gas phase.

and piping lines, and also a hot milk of lime. The effect is cumulative: weak filter liquor and milk of lime require more exhaust steam per ton of soda ash made, which would cause a still larger volume in the distiller waste. When calcium chloride and sodium chloride are to be recovered
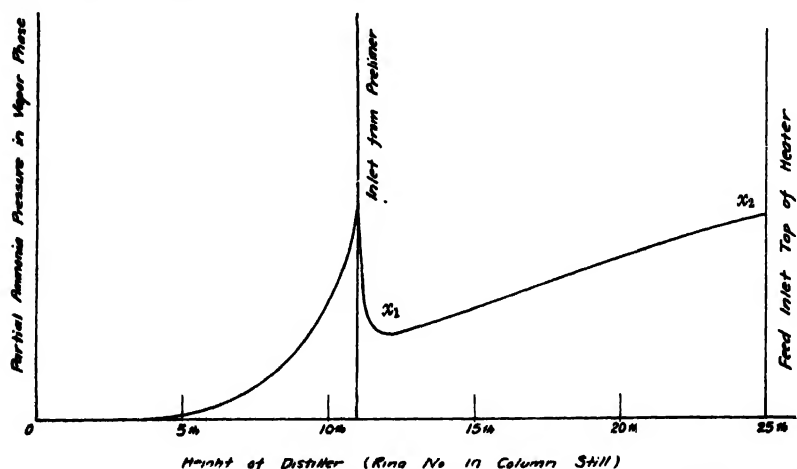
FIG. 70. Curve showing resultant partial pressure of ammonia in gaseous phase.

from the distiller waste, it becomes a *sine qua non* that the distiller waste (and therefore the filter liquor and the milk of lime entering the distiller) should be as concentrated as possible.

To aid in the understanding of the distiller operation, we give a boiling-point table for various concentrations of ammonia in aqueous solutions (Table 99). The values are plotted in Fig. 71.

TABLE 99. Boiling Points of Aqueous Ammonia Solutions of Various Concentrations of Ammonia under Atmospheric Pressure.

NH₃ Per Cent	Boiling Points ° C.	NH₃ Per Cent	Boiling Points ° C.
1	95.6	14	60.3
2	90.0	15	58.3
3	88.3	16	55.9
4	85.0	17	53.9
5	82.2	18	51.7
6	79.4	19	49.7
7	76.6	20	47.5
8	74.2	25	37.2
9	71.6	30	28.0
10	69.2	35	19.75
11	67.0	40	11.67
12	65.0	45	3.33
13	62.5	47.4	0.0

Other design features concerning the efficiency of an ammonia distiller are:

(a) The velocity of the vapor passage through the distiller and the diameter of the distiller.

FIG. 71.

Boiling points vs. per cent by weight of ammonia in solution under 1 atmosphere t o t a l pres-
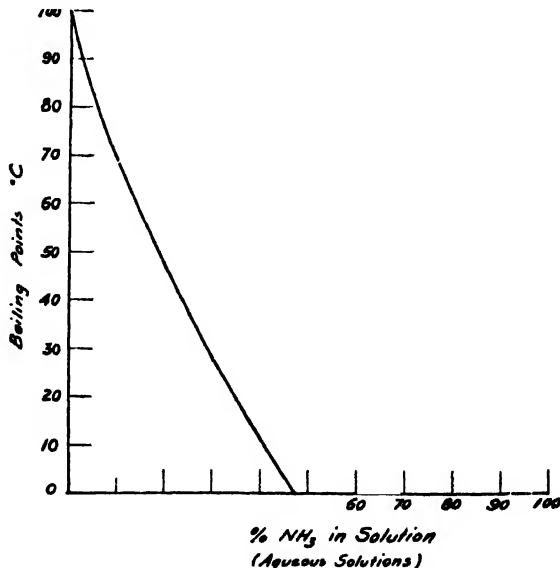
(b) The surface contact between the vapor and the liquor and the agitation of the liquor by steam.

(c) The depth of the liquor on the division plate and the number of passettes.

(a) **Velocity of vapor passage through distiller and diameter of distiller.** Efficiency in the separation of ammonia gas from the liquor is decreased if the liquor on one passette (bubble-cap assembly) is carried up and mixed with the liquor in the other passette above. Such entrainment disturbs the equilbrium relationship between the vapor and the liquid phases. It is generally caused by spattering and splashing of the liquor by steam, and in the worst case the liquor may be "suspended" due to the gas-lock effect of the vapor. Such phenomena are generally caused by excessive velocity of the vapor passing up through the distiller, when the diameter of the distiller is inadequate for the volume of vapor handled. Normally the average vapor velocity from one passette to the other is about 3-6 feet per second, and so the spacing between two adjacent passettes is 2 feet 3 inches on the top to 3 feet 4 inches toward the bottom, with one deepest ring of about 5 feet at the bottom of the lime still where low-pressure steam enters. This is approximately the proportion for an 8-foot distiller. Thus, an 8-foot diameter distiller with standard proportions will under normal conditions have a production capacity of 200-250 tons of soda ash per unit per day, without having too high vapor velocities.

(b) **Surface of contact between vapor and liquor and agitation of liquor by steam.** The lower edge of each mushroom is serrated, so that steam in passing around the edge and bubbling up through the liquor on the division plate may be subdivided and broken up into numerous small bubbles, thus getting more intimate contact with the liquor. Also, the bottom of the division plate, instead of being flat, is best curved to conform to the shape of the path of the flowing steam under the mushroom, so that there may not be any dead spot on the division plate where liquor does not have a chance to come into direct contact with the steam. This helps break up the steam bubbles and stir up liquor body so as to present fresh surfaces of contact between the vapor and the liquid, and to destroy the inactive film layer existing at the liquid-vapor boundary. As the result, the molal fraction of ammonia in the vapor phase approaches more closely the theoretical value in equilibrium with that in the liquid phase on each plate. Further, the overflow outlet is located diametrically opposite the inlet, and the liquor is compelled to travel across the full area of the division plate before leaving the plate. All this results in high efficiency in the performance of each passette.

(c) **Depth of liquor on division plate and number of plates (passettes).** To obtain good contact and effective stirring action, it is necessary that not too large a volume of the liquor, nor too deep a liquor body, is allowed to remain on each division plate. The depth of the liquor on each plate is generally no more than 6 to 7 inches. Contrary to ammonia absorption in the absorber, the depth of wash in the distiller is thus less than that in the corresponding passettes in the absorber. Also the number of passettes in the distiller is larger. The depth of liquor on the plate is controlled by the overflow outlet above the bottom of the plate, while the depth of wash is determined by the submergence of the serrated edge

below the liquor surface. The number of plates (passettes) required may be determined by McCabe and Thiele's graphical method.[*] Take, for example, the lime still. If we determine the molal fraction of NH_3 (1) in the limed liquor fed from the prelimer, (2) in the blow-off, and (3) in the overhead condensate overflowing back to the heater, we can estimate graphically the number of plates required in the lime still, knowing the volume of overflow. However, since the relationship between the lime still and the heater is complicated and the function of the heater is not purely one of rectification, the results so obtained are misleading, and so generally considerably more plates over and above what is theoretically required according to the grapical solution will be needed.

To estimate the quantity of heat to be extracted by the distiller condenser and cooler per ton of soda ash made and the cooling surface necessary, take for example

Distiller top temperature	82° C.
Condenser outlet temperature	56° C.
Total pressure at condenser outlet	754 mm. Hg abs.
Partial pressure steam at 82° C.	385 mm. Hg abs.
Partial pressure NH_3 vapor + CO_2 at 82° C.	369 mm. Hg abs.
Partial pressure steam at 56° C.	123 mm. Hg abs.
Partial pressure NH_3 vapor + CO_2 at 56° C.	631 mm. Hg abs.
Condensate from condenser at 56° C.	16% NH_3
NH_3 in ammoniated brine at 95 titer	80.7 grams per liter
CO_2 in ammoniated brine at 450 cc. per 20 cc.	44.2 grams per liter

Therefore partial pressure of ammonia alone at 82° C. is

$$\frac{\dfrac{80.7}{17}}{\dfrac{80.7}{17} + \dfrac{44.2}{44}} \times 369 = \frac{4.75}{5.75} \times 369 = 305 \text{ mm.}$$

and partial pressure of ammonia alone at 56° C. is (assuming same ratio of NH_3 to CO_2)

$$\frac{4.75}{5.75} \times 631 = 521 \text{ mm.}$$

Therefore the ratio of ammonia to steam in the vapor coming over from the distiller top at 82° C. is as the density of ammonia at 305 mm. is to that of steam at 385 mm. or as 0.0235 lb./ft.^{3}:0.0198 lb./ft.^{3} = 1.186:1. Similarly the ratio of ammonia to steam in the vapor at 56° C. is as the density of ammonia at 521 mm. to that of steam at 123 mm. as 0.0387 lb./ft.$^{-3}$:0.00683 lb./ft.$^{-3}$ = 5.67:1. And the composition of the condensate is 16 per cent ammonia and 84 per cent water, neglecting the carbon dioxide dissolved. At 56° C. per ton of ash there will be:

6.1 cu m. × 80.7 kg. NH_3/cu. m. = 492 kg. NH_3 going into the absorber

[*] McCabe, W. L., and Thiele, E. W., Graphical Design of Fractionating Columns, *Ind. Eng. Chem.*, 17, 605 (1925); and Badger, W. L., and McCabe, W. L., "Elements of Chemical Engineering," pp. 340-372, McGraw-Hill Book Co., Inc., New York, Second Edition, 1936.

or

$$492 \times \frac{6.67}{5.67} = 578 \text{ kg. } NH_3 + \text{steam into the absorber.}$$

Let $W = $ Wt. of condensate in the condenser at 56° C. per ton of ash.

Then

$$0.16W + 578 \times \frac{5.67}{6.67} = (W + 578) \times \frac{1.186}{2.186}$$
$$W = 466 \text{ kg. of condensate}$$

Of this, there are 70 kg. NH_3 and 396 kg. steam.

The quantity of heat to be extracted per ton of ash is:

(1) Heat of condensation of steam at 56° C. at 565
    kg. Cal./kg.
    565×396 .... 224,000 kg. Cal.

(2) Heat of solution of NH_3 in steam condensate at
    8430 cal./mol
    $8430 \times \dfrac{70}{17}$ .... 34,700 kg. Cal.

(3) Heat from cooling of steam from 82° to 56° C.
    at 0.435
    $396 \times 0.435 \times 26$ .... 4,480 kg. Cal.

(4) Heat of cooling NH_3 from 82° to 56° C. at sp.
    ht. = 0.52 $(70 + 492) \times 0.52 \times 26$ .... 7,600 kg. Cal.

Assuming the same proportion of CO_2 in the condensate and ammonia gas from the distiller as being 20% bicarbonated.

(5) Heat of cooling CO_2 gas from 82 to 56° C. at
    sp. ht. = 0.20 $\dfrac{(70 + 492)}{17} \times 44 \times 20\% \times 0.20$
    $\times 26° C. = $ .... 1,510 kg. Cal.

(6) Heat of solution of CO_2
    $(70/80.7) \times (44.2/44) \times 5880$ .... 5,120 kg. Cal.

(7) Heat of neutralization of CO_2 by NH_4OH to
    $(NH_4)_2CO_3$
    $= (70/80.7)\left(\dfrac{44.2}{44}\right) \times 16,850$ .... 14,650 kg. Cal.

Total heat to be extracted .... 292,000 kg. Cal. per ton of ash

Among the various cooling duties to be performed in the soda ash plants, such as in the absorber coolers, vat coolers, carbonating tower cooling boxes, furnace condensers, etc., the cooling duty of the distiller condensers is one of the most important and should require provision for one of the largest cooling surfaces in the whole equipment. Fortunately, the mean temperature difference for the flow of heat from the condensing vapor to the cooling water is generally great. Thus, suppose the temperature of the ammonia gases is 82° C. and it is desired to cool the gases to 56° C. Suppose the cooling water has a temperature of 20° C. and is warmed to 40° C at the exit. The mean temperature difference then is

$$\frac{(82 - 40) - (56 - 20)}{2.3 \log \left\{ \dfrac{42}{36} \right.} = \frac{6}{2.3 \log 1.167} = \frac{6}{2.3 \times .0671} = 38.9° C.$$

The heat transfer from condensing steam to water should also be favorable. It is, however, very difficult to calculate exactly the cooling surface required because the coefficient of heat transfer depends largely upon the tube conditions both inside and outside. An insulating layer of ammonium carbonate crystals, iron scale, etc., on the vapor side of the cooling tubes, and a hard scale formed from the hardness or mud in the cooling water on the water side are liable to be formed. These would greatly reduce the rate of heat flow from the condensing steam to the cooling water.

The specific gravity readings (at room temperature) of different liquors are given in Table 100.

TABLE 100. Specific Gravity of Different Liquors.

Crude saturated sea brine	1.205-1.210
Saturated rock salt brine	1.195-1.200
Ammoniated brine	1.165-1.175 (depending upon CO_2 content)
Precarbonated liquor	1.220-1.230 (depending upon CO_2 content)
Draw liquor	1.126-1.127 (depending upon tower decomposition)
Distiller waste liquor	1.100-1.130 (depending upon filter liquor volume, etc.)

Between the distiller top outlet and absorber bottom inlet, the temperature of the ammonia gases should drop from about 86 to 56° C. In other words, the distiller condensers and coolers should have sufficient capacity to cool the hot ammonia gases coming from the heater by about 30° C. As a rough guide there should be 70 square feet of total cooling surface in the distiller coolers and condensers combined per ton of soda ash made per day.

Following is an estimation of the exhaust steam required in the distillers. For the estimation of steam required in the distiller per ton of soda ash made. not all the necessary data are available; some assumptions must be based on practical observations. We shall assume, in the absence of the specific figures available, that the heat effect of the neutralization of the first hydrogen of the carbonic acid by ammonia is 11,000 cal. per mol. Next, we shall place the figure for heat loss by radiation from the well-lagged distiller at 10 per cent of the total heat required per ton of ash. We shall take the following set of data:

Vol. of feed liquor per ton of ash	7,000 liters
Vol. of milk of lime required per ton of ash..........	2,500 liters
Free ammonia (NH_4HCO_3) per ton of ash	150 kg. NH_3
Fixed NH_3 (NH_4Cl) per ton of ash	350 kg. NH_3
CO_2 dissolved in the liquor	39 grams per liter
Heat of neutralization	
$NH_3 . Aq + H_2O + CO_2 . Aq \rightarrow NH_4HCO_3 . Aq + Q$	
$Q = 11,000$ cal./mol NH_3	647 cal./gram
Heat of solution of NH_3	8,430 cal./mol
Heat of solution of CO_2	5,880 cal./mol
Exhaust steam at 10 lbs. gage (115° C.) from steam at 10 lbs. to water at 10 lbs.	529 cal./gram
Temperature of feed liquor to distiller	45° C.
Temperature of milk of lime	55° C.

Then,

$$7000 \text{ l.} \times (115° - 45° \text{ C.}) = 7000 \times 70 \quad \text{..................} \quad 490{,}000 \text{ kg. Cal.}$$

$$2500 \text{ l.} \times (115° - 55° \text{ C.}) = 2500 \times 60 \quad \text{..................} \quad 150{,}000 \text{ kg. Cal.}$$

Heat of decomposition of 150 kg. NH_3 from NH_4HCO_3
$$= 150 \times 647 \quad \text{.....................................} \quad 97{,}050 \text{ kg. Cal.}$$

Heat to drive 150 kg. NH_3 from solution $= 150 \times \dfrac{8430}{17} \ldots \quad 74{,}400 \text{ kg. Cal.}$

Heat to drive 39 kg. CO_2 from solution $= 39 \times \dfrac{5880}{44} \times 7000 \quad 36{,}500 \text{ kg. Cal.}$

Heat to drive 350 kg. NH_3 from fixed NH_3 and CaO
$$= 350 \times \frac{8430}{17} \quad \text{.......................................} \quad 173{,}560 \text{ kg. Cal.}$$

Total	1,021,500 kg. Cal.
Heat loss by radiation at 10% ....,..............	102,150 kg. Cal.
Total heat required	1,123,650 kg. Cal.

Exhaust steam required $\dfrac{1{,}123{,}650}{529}$ ....2.12 cu. m. (as condensate water)

Note that the heat of reaction for the 350 kg. NH_3 in the following reaction is negligible, because it is an equilibrium reaction with all components in solution:

$$2NH_4Cl \cdot Aq + Ca(OH)_2 \cdot Aq = CaCl_2 \cdot Aq + 2NH_4OH \cdot Aq + Q$$
$$(-72{,}800 \times 2) \quad (-244{,}200) \quad (-214{,}000) \quad (-88{,}000 \times 2)$$
$$\therefore Q \text{ is negligible.}$$
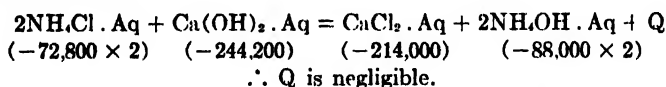
That is, the heat effect in the above equilibrium reaction may be neglected.

From the above it will be seen that the greatest item of heat required is that required to heat up the liquors. This takes 64 per cent of the total heat required. Therefore, for good efficiency, the feed liquor and the milk of lime must be preheated and kept hot and be as concentrated as possible. The exhaust steam to the distiller must be dry, *i.e.*, the condensate in it must be previously completely separated out. In practice, the smaller the volume of the filtered liquor and of the milk of lime, the smaller will be the amount of exhaust steam required for distillation, and consequently the smaller the volume of the distiller waste, and the smaller the losses of both ammonia and lime in the distiller waste sent out.

Chapter XV
By-products from Distiller Waste

The distiller run-off liquor consists of some 85 grams per liter of calcium chloride, 50 grams per liter of sodium chloride, and some excess of lime, together with other solid matter such as silicious matter, calcium carbonate, magnesia, calcium sulfate, etc. The concentration of these constituents varies widely in individual plants depending upon the operating conditions and upon the efficiency of the plant. The liquor contains all the chlorine from the salt used; for, unlike the LeBlanc process, the ammonia process makes no use of the chlorine. Because of the high cost of the fuel required to concentrate such a weak liquor, and because of the limited demand for calcium chloride and the cheapness of this product, and salt, comparatively little of this distiller waste has been worked up, considering the very large volume of the waste turned out daily by the ammonium soda industry.

The solid matter from the waste accumulates so fast that the disposal of this waste is a matter of no small concern to ammonia soda manufacturers. Calcium chloride in solution permeates the soil bed and contaminates sources of water supply. Municipal authorities permit only a very limited portion of the waste (except the clear portion of the liquid) to be sent to a river or any public waterway, and that only after complete settling to eliminate the solids. Cases are on record where fish in the river were killed by the harmful constituents, especially the free lime carried in the liquor, so that ammonia soda manufacturers are obliged to do something to this waste. Proposals have been made to utilize it in many different ways, and various products have been claimed to have been prepared therefrom. Many of these proposals have no practical value. The preparation of chlorine gas (from which bleaching powder is made) or the production of hydrochloric acid from the calcium chloride in the waste by electrolysis can no longer be considered practicable in view of the present much more economical methods for preparing these products.

There is a considerable excess of unconverted salt in the waste. It must be said that the ammonia soda process is very wasteful in the use of salt, the average efficiency in conversion of salt to sodium bicarbonate in the carbonating towers in actual operation being not more than 75 per cent; considering some additional losses in the form of "mud" pumped to the distiller, more than 25 per cent of the total salt is wasted. As a consequence, the very existence of an ammonia soda works presupposes a cheap and abundant supply of salt. Because of this fact it generally does not pay to recover this salt from distiller waste. The salt so recovered,

however, possesses a high degree of purity and is comparable to the product obtained from brine purified by the soda-lime treatment. This salt is recovered in conjunction with the manufacture of calcium chloride.

We shall enumerate a few of the principal products that have been prepared from distiller waste on a commercial scale; namely, refined salt, calcium chloride, calcium sulfate, and ammonium chloride.

Refined salt and calcium chloride. It is the aim of ammonia soda operators to keep the volume of distiller waste as small as possible, especially when any of it is to be worked up. This is done by keeping the volume of the filter liquor as small as possible, by securing the highest decomposition possible in the columns, by using as little wash water on the filters as is necessary to reduce the sodium chloride content in the ash within allowable limits, and by employing a strong milk of lime containing not less than 250 grams of lime per liter (sp. gr. 1.21). In certain cases even solid lime has been tried in the preliming tanks for distiller operation. This waste liquor, which contains a small excess of free lime as mentioned above, is carbonated by passing some waste CO_2 gases through it. On settling, the precipitated calcium carbonate and all the solid matter, such as magnesia, silica, calcium sulfate, etc., carried in the liquor separate out. The clear solution containing calcium chloride, sodium chloride, and a very small proportion of dissolved calcium sulfate, is concentrated in a double-effect evaporator, when sodium chloride together with the small amount of calcium sulfate commences to crystallize out. The salt crystals are dried in centrifuges, a little water being sprayed on them to wash any calcium chloride from the salt. From the centrifuges the salt can be packed directly in bags of 200 pounds or in barrels of 400 pounds, frequently without further drying. If drying is necessary, the salt from the centrifuges or drum filters is charged to steam-heated, hot-air rotary dryers using exhaust steam.

The liquor entering the evaporator with a specific gravity of 1.11 is concentrated to 1.22 in the first effect, and evaporation is carried on until the specific gravity of the liquor in the last effect is 1.42. At this point practically all the salt can be settled out.

If necessary, some "chloride of lime" may be added to oxidize the iron and the liquor is then allowed to settle. The liquor should not be allowed to cool too much, or hexahydrate calcium chloride crystals ($CaCl_2 . 6H_2O$) would separate out. This clarified calcium chloride liquor containing 42 to 45 per cent calcium chloride is known in commerce as "liquid calcium chloride." It is shipped in tank cars like liquid caustic. It is used in refrigerating plants, for road sprinkling, and for making liquid concrete accelerators.   •

· If solid or flake calcium chloride is desired, the clarified liquor may be further concentrated in cast-iron open pots until the molten mass, solidifying on cooling, gives what is known as 75-per cent calcium chloride, corresponding to the formula $CaCl_2 . 2H_2O$. A more recent method is to use a high-pressure, single-effect evaporator to concentrate this 1.42 sp. gr. liquor directly to 75-per cent calcium chloride, using a higher pres-

sure steam instead of the exhaust. The heat economy in the evaporators is far greater than in the cast-iron open pots. This product in the molten state is pumped to steel drums, each holding about 650 lbs., and the drums are sealed. The composition of 75-per cent solid calcium chloride is given in Table 101.

TABLE 101. Composition of 75-per cent Calcium Chloride.

	Per Cent
$CaCl_2$	73.6
NaCl	1.4
Alkalinity as $Ca(OH)_2$	0.14
Insoluble matter	0.08
Water by difference	24.78

Flaked calcium chloride is made by sending the 75-per cent molten calcium chloride to flaking machines provided with revolving water-cooled drums, as in flake caustic manufacture.

Anhydrous calcium chloride can be made by heating 75-per cent calcium chloride in a reverberatory or puddling furnace, fired by producer gas or oil. The molten mass is frequently raked, when some calcium chloride is decomposed, giving lime and hydrogen chloride. The escape of this hydrogen chloride gas leaves a porous mass of fused calcium chloride, which is known as 95-per cent $CaCl_2$. The cooled anhydrous mass, somewhat fluorescent, is packed in steel drums or paper-lined wooden barrels, hermetically sealed, each holding from 350 to 400 pounds.

Fused calcium chloride, like fused caustic soda, has a density of about 2 (sp. gr. of anhydrous $CaCl_2$, 2.22); but unlike caustic soda the melting point is much higher (775° C.). Hence molten anhydrous calcium chloride could not be readily obtained in fusion pots, as is the case with fused caustic soda.

There is a process for making powdered calcium chloride by drying the granular calcium chloride in a rotary furnace by means of furnace gases entering at 400 to 475° C. and leaving at 100° C. The coarse particles drop out of the lower end of the rotary, while the fine dust suspended in the current passes out of the upper end and is recovered in a collector containing about 73 per cent anhydrous calcium chloride, which is non-caking.

Calcium chloride is used as a refrigerant in the manufacture of ice, as a dust palliative in flake or granular form to minimize dusts on gravel roads, and as an anti-freezing solution (freezing point −50° F.) In the anhydrous form small quantities are used as a catalyst to promote the reaction between calcium carbide and nitrogen gas in the manufacture of calcium cyanamide, permitting a lower temperature to be employed.

Calcium sulfate. The crystalline $CaSO_4 . 2H_2O$ is known as "Crown Filler" among the Solvay products. It is a much purer product than natural gypsum. The process of manufacture consists in settling the distiller waste and treating the settled liquor while still hot with salt cake. The excess of free lime carried in the liquor will be neutralized by the slight excess of sulfuric acid in the salt cake. If the resulting solution is acid, some milk of lime may be added. The precipitated $CaSO_4 . 2H_2O$

in finely divided form is filtered on a vacuum drum filter and further dried in a centrifuge, water being sprinkled on the crystals to wash away salt. The crystals of gypsum are dried at a reduced temperature in much the same way as sodium bicarbonate (see Chapter XVIII). It is packed in wooden barrels of about 350 to 400 pounds and used as a paper filler. A small quantity is used as a water hardener in the fermentation industries.

When dried at or below 190° C., this gives plaster of Paris ($CaSO_4 . \frac{1}{2}H_2O$) which is used for making molds. When calcined at a temperature above 204° C. it loses all its water, care being taken that none of the sulfate is reduced to sulfide. When traces of iron are present, the calcined mass is discolored and gives a yellow tint.

Calcined calcium sulfate is used in the manufacture of certain tooth pastes and in the manufacture of wall and flooring plasters which give a smooth and hard finish.

The filtered liquor, after removal of the precipitated calcium sulfate, is a very pure brine which is sent to the soda works for making saturated brine for soda manufacture.

Ammonium chloride. In this connection may be mentioned sal ammoniac (ammonium chloride), which can be obtained by concentrating the carbonated and settled waste liquor to remove most of the salt (NaCl) and treating it with ammonium sulfate $(NH_4)_2SO_4$, whereby the following reaction takes place:

$$CaCl_2 + (NH_4)_2SO_4 \rightarrow CaSO_4 + 2NH_4Cl$$
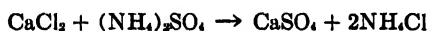
The mother liquor is further concentrated, allowed to settle, and cooled. Crystals of ammonium chloride then separate out. This process was originally patented by Richardson.

Another process proposed for the manufacture of sal ammoniac that may involve important changes in the ammonia soda industry is as follows: From the mother liquor (or filter liquor) before distillation, it is proposed to separate ammonium chloride by cooling. This was done in Germany during the World War by the Badische Anilin- und Soda-Fabrik using synthetic ammonia. In Japan it was claimed that by freezing out ammonium chloride from the mother liquor and by adding a fresh supply of salt, the resulting liquor can be sent back to the carbonating towers for making sodium bicarbonate, thus doing away with distillation. It is claimed that in this way the distiller can be dispensed with and the operation in the ammonia soda works simplified.

The detailed procedure consists of introducing more ammonia and salt to the mother liquor after filtration and carbonating the resulting liquor again to throw out more sodium bicarbonate, using a rather low temperature. The bicarbonate is filtered off as usual, and the mother liquor, which is now very rich in ammonium chloride, is strongly cooled so that ammonium chloride crystals separate out. The crystals are then centrifuged and washed in the usual manner.

Solvay makes a large amount of ammonium chloride—more than 50 or 60 tons a day. It is made from distiller waste liquor by first settling off the solids from the liquor and concentrating the solution in evaporators. The small percentage of lime remaining dissolved in the solution up to about 2 grams per liter makes calcium chloride liquor less corrosive on evaporators. The solution is concentrated to 40° Bé., containing about 40 per cent $CaCl_2$, when most of the salt separates out. The slurry containing salt crystals is filtered off and the filter liquor ammoniated. The ammoniacal calcium chloride solution is then carbonated in tanks at a temperature of 60° C. with stirrers; at this point very coarse calcium carbonate crystals are formed, which filter very readily, and the filtrate containing high concentration of ammonium chloride is cooled when the ammonium chloride crystals begin to separate.

$$CaCl_2 + 2NH_3 + CO_2 + H_2O \rightarrow CaCO_3 + 2NH_4Cl$$
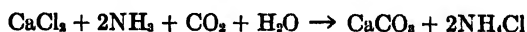
The liquor is then concentrated so that further crops of ammonium chloride crystals are obtained. Solvay at first used wooden tank filters with false bottoms for such purpose, although ordinary filters work very successfully. Ammonium chloride crystals made in this way contain only 0.3 to 0.4 per cent sodium chloride.

The ammonium chloride crystals are dried with hot air at a low temperature. The same equipment as is used for drying refined sodium bicarbonate is suitable for this purpose. (See Chapter XVIII, Manufacture of Refined Sodium Bicarbonate.)

This process of making ammonium chloride runs exactly parallel to the gypsum process of making ammonium sulfate used by I. G. Farbenindustrie in Ludwigshaven-Oppau, Germany, the differences being that calcium chloride is used in place of calcium sulfate, and that ammonium chloride is obtained instead of ammonium sulfate.

Ammonium chloride is used in the manufacture of dry cell batteries and in metal working for soldering and galvanizing. For this purpose, a mimimum purity of 99.2-99.4 per cent NH_4Cl is required; whereas for fertilizer, anything above 97 per cent NH_4Cl is acceptable, the impurities being mostly NaCl.

Soil Lime. Solids carried in the waste liquor, consisting of waste sand, finely divided calcium carbonate, excess lime, calcium sulfate, magnesia, etc., are allowed to separate by settling, and the sludge is sometimes used as "fertilizer" for correcting acidic soil. However, the calcium chloride content of the waste lime should be allowed to weather and be washed off by rain before it is applied to farms. What fertilizing value it has is difficult to determine, but some farmers do use this waste sludge on their farms with favorable results.

An ammonia soda plant is considered to be happily situated if it can send its distiller waste to the neighboring lands freely. If a plant is situated among quarry hills where the distiller waste can be sent to fill the quarry pits or the adjoining valleys, or if a plant can be situated near

the sea or on a large lake to which distiller waste can be discharged freely, the situation approaches an ideal one. For the time is still far distant when such waste, which is produced daily in enormous quantities, can all be worked up into by-products. The great bulk of waste must be disposed of and the space for its disposal must receive attention from ammonia soda manufacturers at the outset.

Distiller waste accumulated in the neighborhood of an ammonia soda plant leaves a rather unsightly feature in our landscape. In the course of years, after weathering has set in, green vegetation will grow on it. The muck may then become a good farm land again.

Chapter XVI
Alkali Products of Ammonia Soda Industry

Besides the products naturally allied to soda ash, namely chemical caustic and refined bicarbonate, ammonia soda manufacturers make many miscellaneous products from the combination of soda ash, caustic soda, sodium bicarbonate, etc., to meet special needs of certain industries. The manufacture of these products in most cases involves no special technical operations, but it helps the manufacturers to sell their products, as they claim to be specially prepared to meet the specific needs of certain classes of consumers.

In this chapter we shall not include those products known as by-products from distiller waste, such as calcium chloride (liquid, solid or flake), refined salt, calcium sulfate, etc., which are dealt with in Chapter XV, "By-products from Distiller Waste." We shall consider only those special names in the trade catalogs of the ammonia soda manufacturers.

Extra Light Ash, "Fluf," or Fluffy Soda. This is a very loose and bulky form of light ash, desired by a certain class of household suppliers who would like to have large bulk for their packages. It has the advantage of dissolving more easily. This product is generally collected from cyclone separators or dust collectors at the drying and finishing end of the process. The quantity available is therefore not large. It has a specific gravity of about 23 pounds per cubic foot.

Light Ash. This is ordinary soda ash obtained directly from the calcining of the filtered bicarbonate in the rotary dryers, or in Thelen pans. Because of the violent agitation in the carbonating towers by the bubbling action of the CO_2 gas, the crystals of $NaHCO_3$ formed are necessarily very fine; thus the soda ash obtained from the calcination of these crystals is loose and fine. It occupies a comparatively large volume per unit weight, and its specific gravity is only about 35 pounds per cubic foot. The density of the light ash varies a great deal, depending upon the character of the bicarbonate crystals from the columns, the moisture content of the bicarbonate, and the method of calcining it. Soda ash is now added to the clay mix in small quantities in the manufacture of firebrick, etc.

Modified Sodas. These are various mechanical mixtures of sodium bicarbonate ($NaHCO_3$) and soda ash (Na_2CO_3) in ratios varying from 25 to 75 per cent sodium bicarbonate by weight. They are also called "neutral sodas," and are used where a milder alkali is desired. Depending upon the percentage of sodium bicarbonate admixed, they are sold under different names allegedly to meet specific needs of certain indus-

tries. "Tanners' Soda," "Textile Soda," "Laundry Soda," etc., come under this group.

Sodium Sesquicarbonate. This is a special form of "neutral soda." It is a double salt having the formula $Na_2CO_3 . NaHCO_3 . 2H_2O$, and hence has a definite composition and crystalline structure. It consists of fine, lustrous, needle-like crystals. The product is known as "Concentrated Crystal Soda" in England, but as "Snow Flake Crystals" among the Solvay products in America. In its natural state it is known as "trona" or "urao." It is a stable compound, neither hydroscopic like soda ash, nor effervescent like sal soda; and it does not form lumps on storing. It is readily soluble in water and dissolves without evolution of heat like soda ash (Na_2CO_3) or monohydrate ($Na_2CO_3 . H_2O$), and without absorption of heat like sal soda ($Na_2CO_3 . 10H_2O$). This compound exists extensively in natural soda deposits, as it is the ultimate stable form of sodium carbonate in contact with the atmosphere.

The crystals can be manufactured by adding an excess of sodium bicarbonate to a hot soda ash solution somewhat above the ratio of 84 parts $NaHCO_3$ to 53 parts soda ash by weight. The resulting strong solution is allowed to cool slowly, whereupon fine, shiny crystals are formed.

There is a process for making refined sodium bicarbonate from the crude bicarbonate by dissolving the latter hot, distilling off the ammonia as in the distiller operation but without addition of lime, settling the solution, cooling, and finally recarbonating the cooled, settled liquor as in the ammonia soda operation. During distillation, a considerable portion of the bicarbonate is decomposed to normal carbonate; and by close regulation, just enough sodium bicarbonate can be decomposed to form normal carbonate so that the resulting solution is of the right composition to form sodium sesquicarbonate crystals by cooling and recrystallization.

Again, sesquicarbonate may be made by dissolving soda ash, recarbonating with lean gas (weak CO_2 gas) in a wooden tower to a proper degree of bicarbonation, and then cooling the solution to crystallize out the sesquicarbonate crystals. One of the natural soda manufacturers in California partially carbonates soda brine to precipitate sodium sesquicarbonate this way.

The crystals of sodium sesquicarbonate are dried at a reduced temperature in the same type of equipment as the sodium bicarbonate dryer, and are packed in wooden barrels containing 280 lbs., or in kegs containing 85 lbs. each. The sesquicarbonate, being stable, is not affected by atmospheric moisture or CO_2 and is therefore free from lumps. It is readily soluble and finds much favor in wool scouring and laundering.

Granular Sodium Carbonate or Crystal Carbonate. This is the monohydrate of soda ($Na_2CO_3 . H_2O$) and is obtained by crystallization from solution like sal soda, but at a very much higher temperature. Theoretically, a temperature above 35° C. will yield these crystals: in practice a boiling temperature is employed because of the ease of concentrating the solution. This is a fairly stable compound to which sal soda is first con-

verted, on exposure, in the form of a white outside crust. Natural sal soda deposits yield this white powder on the surface layer by efflorescence. In the natural state it is known as thermonatrite, $Na_2CO_3 . H_2O$. By absorption of CO_2 and moisture from the air, crystal carbonate finally goes over to the sesquicarbonate ($Na_2CO_3 . NaHCO_3 . 2H_2O$). Hence the preponderating proportions of the latter in natural soda deposits.

Crystal carbonate is first formed when soda is recovered from burkeite ($Na_2CO_3 . 2Na_2SO_4$) in the plant of the American Potash & Chemical Corp. at Trona on Searles Lake. It is then calcined to dense ash.

Sal Soda. Sal soda, washing soda, or soda crystals is the decahydrate of sodium carbonate ($Na_2CO_3 . 10H_2O$) occurring in nature as "natron." The crystals are formed from solution at a temperature below 32° C. In the old days, when pure soda could not be obtained from the LeBlanc process, people preferred to use soda crystals to avoid having caustic in the soda and to insure getting a purer product. It was used in washing and in the scouring of wool. Nowadays a very pure soda ash can be obtained from the ammonia soda process, and the trade in this article has greatly declined on account of its high freight cost and the difficulty of keeping the crystals in hot weather. These crystals contain more than 60 per cent of their weight of water and dissolve in their own water of crystallization in tropical climates. Sal soda manufacture requires a large floor space. When the solution is prepared from the ammonia soda, a tank provided with a stirrer much like the causticizing tank is used. Water is heated, to which soda ash together with the desired amount of sodium sulfate is added (see below) until its specific gravity shows 36° Bé. at this temperature. This will take about 50 per cent soda ash on the weight of water. To aid solution, however, the liquor is heated by closed steam coils to 60 to 70° C., and while settling and clarifying must be kept above 50° C. to prevent its crystallization and clogging of pipes, etc. For this reason, the reservoirs, pipes, etc., should be lagged. After all has been dissolved, the stirrer is stopped, the solution allowed to settle, and the clear portion drawn into shallow crystallizing pans. These are 10 feet wide by 10 feet long by 2 feet deep from the top to the pyramid bottom. On reaching the pans, the solution should have been cooled to about 32° C. The pans are set on brick or concrete piers so that the mother liquor can be drawn from the bottom. They are set aside to crystallize for 4 to 10 days, depending upon the size of the pan, the weather conditions, etc. On hot summer days this operation is attended with great difficulty. Across the pans are suspended galvanized iron wire nettings with strings or wires barely submerged under the surface of the liquor. Crystals are formed hanging from these wires immersed in the liquor. After crystallization, the mother liquor shows a Bé. reading of only 20 to 22° when it is drawn off. The crystals formed on the sides and bottom are chiselled off and charged to centrifuges to whiz out the enclosed mother liquor. A little fresh water is sprayed on the centrifuge to wash out the remaining mother liquor. The crystals are broken up in an impact crusher and packed in wooden barrels, each containing **280 lbs.**

Instead of the dissolving tanks described above, a small rotary dissolver with angle-iron flights riveted on the shell inside gives continuous operation and has a very large capacity, the solution being settled in a separate tank outside.

The manufacture of sal soda possesses some advantage in that discolored soda ash and floor sweepings can be dissolved and utilized for its manufacture. In this case the solution must be well settled and decanted from the dirt. Thousands of tons of red soda produced when starting a new ammonia soda plant have been utilized in this way or in the manufacture of caustic soda.

In order to obtain larger crystals from ammonia soda, anhydrous sodium sulfate is added with the soda ash to the extent of 2.5 to 3.0 per cent by weight. This, of course, contaminates the product but the users generally do not object to it.

Sal soda is made more extensively by natural soda manufacturers who purify the natural soda deposits by redissolving and recrystallization, yielding sal soda crystals ($Na_2CO_3 . 10H_2O$) or crystal carbonate ($Na_2CO_3 . H_2O$).

Block Soda. In the Orient, much soda is handled in block form. Large quantities of soda ash are made into blocks and sold in this form, because of the old practice in which natural soda was handled. Soda ash in a finely powdered form has a tendency to "set" in contact with water when the mass is not disturbed by stirring, and further will unite with a considerable amount of water, maintaining its firm, solid form when cooled. From fresh ammonia ash in a finely divided state which has not absorbed any moisture by exposure, a suspension, or thin paste, formed by stirring the fine powder into as much as 135 per cent of its weight of water, will "set" to a firm, solid form on cooling. The amount of water the soda will take in this way depends upon (1) percentage of Na_2CO_3 (not as $NaHCO_3$) in the ash, (2) the fineness of the crystals, and (3) the weather conditions. The ability to absorb water and form a firm, solid block is materially impaired if soda ash has in part been already converted to $NaHCO_3$, or if it has absorbed much moisture from the air through long storage or after transportation over a long distance. To make these blocks, soda ash is screened and the coarser particles or lumps are pulverized until all pass through at least a 20-mesh screen. The powder is gradually stirred into 100 to 135 per cent of its weight of water at about 30° C. and the mixture continuously stirred. This stirring operation is very important and serves to mix the ash thoroughly with water. As it is stirred, the suspension gradually becomes thick. Stirring is continued until the suspension thickens to the consistency of a starch paste, whereupon it is transferred to wooden molds, 34 inches long by 14 inches wide by 8 inches deep (inside dimensions), and allowed to "set" for 24 to 36 hours, after which the blocks formed can be taken out by loosening the sides of the molds.

Some sodium bicarbonate is added to the paste toward the end of the stirring just before pouring into forms, especially in summer. This serves

to hasten the "setting" time by "seeding" and to give better grain appearance in its cross-section. The amount of sodium bicarbonate required is 2 to 2½ per cent in winter and 3 to 5 per cent in summer, based on the weight of soda ash taken. The blocks will thus analyze less than 50 per cent Na_2CO_3. A typical analysis is given in Table 102.

TABLE 102.   Composition of Block Soda.

	Per Cent
Na_2CO_3	46.12
$NaHCO_3$	2.90
$NaCl$	0.56
Insoluble matter	0.33
Water	50.07

In the East, soda in this form, or in the decahydrate form, is used in making steamed bread, noodles, cakes, fryings, etc., and also in washing.

Causticized Ash or "Super Alkalies." These are various mechanical mixtures of caustic soda and soda ash containing 10 to 50 per cent by weight of caustic soda. They are put up to meet those requirements in certain industries where a stronger alkali is desired. Depending upon the percentage of caustic soda admixed, they are sold under different names, such as "Tanners' Alkali," "Bottlers' Alkali," "Metal Cleaning Alkali," "Creamery Alkali," "Boiler Compounds," etc.

Dense Ash. The old LeBlanc industry produced a heavy form of soda ash, more than twice as dense as ordinary ammonia soda ash. Certain manufacturers (such as glass and ultramarine makers) objected to this loose form of product, and ammonia soda manufacturers, in attempting to meet their requirements, at first re-fired the ordinary ash in a reverberatory (or gas-fired, down-flame) furnace to incipient fusion to bring up its density. The present method, however, is to add a proper percentage of water to the ordinary ash, mix it thoroughly, and re-dry it in a rotary dryer. Hence also the name "water ash." Its density can be increased by 80 to 95 per cent over the light ash. This increase in density also materially reduces the cost of packing material per unit weight. It is generally divided into two classes: the medium dense, weighing about 50 lbs. per cu. ft. and the heavy dense, weighing about 65 lbs. or more per cu. ft.

Granular Ash. This is a coarse-grained, heavy, dense ash made by employing a rather high percentage of water and drying. The product is sized by screening and the coarse particles on the screen give the "granular ash." Its dustless property is much favored by the glass industry.

Fused Soda Ash. Soda ash has valuable properties as the alkali material required for metallurgical processes, such as purification of molten iron and analogous operations. Light ash, or other form of dry sodium carbonate, is fed into a refractory-lined furnace through suitable charging openings in the roof. The furnaces are fired with either fuel oil or pulverized coal directly over the hearth into which the soda ash is being fed. The soda ash melts (m.p. 1564° F.) and maintains a level in

the hearth of the furnace above the run-off spout. The stream of molten soda is cast into iron molds carried on carts or a continuous chain. The castings of soda ash are dumped out of the pans as soon as frozen and allowed to cool. They are shipped either in bulk or in cartons of one kind or another. The actual temperature of casting is about 1600 to 1650° F. The low latent heat of fusion and the low specific heat cause rapid freezing and cooling.

When the product is being made with a pulverized-fuel fire, the blocks become contaminated with the ash of the fuel. For many purposes to which this form of alkali is put, there is no objection to such contamination. For other purposes the oil- or gas-fired furnace product is made.

The physical form, the weight of block and the composition are all varied to suit customers and specific uses. In the iron foundry business three-pound blocks of uncompounded fused soda ash have become more or less standard. For laundry work, dairy uses, etc., other sizes and shapes are marketed. Manufacturers of water-treatment chemicals require blocks compounded with phosphorus, etc. Other special users request tinted blocks. The smallest block on the market is about one-half pound and the largest is four pounds. Soda ash is also fused with sulfur for feeding into a waste liquor calciner in kraft paper manufacture.

A type of globular dense ash has been made by melting the light ash and atomizing it by means of compressed air into an insulated chamber lined with refractory material. This gives small globules of soda ash which is much denser—even denser than "water ash"—and is particularly dustless for glass manufacture.

Ammonium Carbonate. This product is made by passing carbon dioxide gas through an aqueous solution of ammonia in a still. The gases consisting of ammonia, CO_2, and water vapor are distilled off and condensed in a water-cooled condenser and caused to solidify to a dense, crystalline mass. The mass is then passed through steel circular saws in directions at right angles to each other, forming $\frac{3}{4}$-inch cubes. These ammonium carbonate cubes are used as "smelling salts" and for other medicinal purposes. They are among the common chemicals in chemical laboratories and are also employed as baking powder. Such crystals of ammonium "carbonate" generally contain also ammonium carbamate and ammonium bicarbonate.

Ammonium Bicarbonate. This product is obtained by carbonating the ammonia solution in a tower much in the same way as in the precipitation of sodium bicarbonate from the ammoniated brine. The fairly soluble salt of ammonium bicarbonate, which is analogous to sodium bicarbonate, is rendered difficultly soluble in the presence of the excess reagents in solution, separates out as fine crystals, and is filtered and centrifuged in the same way. The fine crystals are dried by hot air at a temperature of about 50° C. on belt conveyors in a closed chamber heated by steam coils. The dried crystals finally leave the belt as fine powder which is then elevated, screened, and packed in paper-lined wooden barrels, or, in small sizes, in paper boxes. These ammonium bicarbonate

crystals are used as a valuable baking powder which yields carbon dioxide and ammonia gases copiously but which leaves no residue in the bread as do the other kinds of baking powder. Ammonium bicarbonate may also be used as fertilizer.

In the Solvay Works not so much ammonium bicarbonate is made because of its limited use—only 5 tons being made a day. What is made, however, is very pure and free from iron. For this purpose a 26° Bé. aqua ammonia containing about 29 per cent of NH_3 is used. This is a refined aqua ammonia in which hydrogen sulfide has been removed by redistillation. It is made by running crude aqua ammonia through a distiller and passing the ammonia vapor through a water scrubber or condenser in which hydrogen sulfide is washed down by the down-stream of water in the partial condenser.

In the Solvay practice, this 26° Bé. refined aqua ammonia is run through a very small tower—much smaller than the standard Solvay tower—and lean gas (or kiln gas) is passed through the tower, with a certain amount of cooling, so that the slurry is kept at about 25° C. The slurry contains about 25 per cent crystals. Wooden tank filters with false bottoms are used to filter these bicarbonate crystals so that no iron will be picked up from the filters. At 25° C., these crystals, though having high vapor pressure, lose ammonia only very slightly. But above 36° C. the vapor pressure becomes excessive and decomposition of the ammonium bicarbonate crystals into ammonia and CO_2 is active.

In the ammonia soda plants, it is best to pre-carbonate the aqua in a separate tower and precipitate the bicarbonate in the making tower. In this way the precarbonating tower containing the normal ammonium carbonate solution is not subjected to corrosion, all the corrosion occurring in the making tower. Only lean gas or kiln gas is used in these towers. Old discarded Solvay towers can be used for such purpose; but if no iron can be tolerated in the ammonium bicarbonate, wooden towers are constructed for this purpose.

Ammonium bicarbonate crystals are generally bigger than ammonia soda crystals and easy to filter, but Solvay use exclusively open wooden tank filters because the amount made is small and the loss of ammonia due to exposure is not excessive. Standard rotary filters or centrifuges also work satisfactorily.

Because of high vapor tension, ammonium bicarbonate decomposes very readily into CO_2 and NH_3. Hence only air-tight containers can be used. Lately a very stable crystalline form of ammonium bicarbonate has been prepared by the workers of the Gesellschaft für Kohlentechnik, Germany, and it is claimed that such crystals of ammonium bicarbonate could be packed in gunny bags and transported or stored in these bags for months without material loss by decomposition.

Ammonium Chloride. This can be obtained from the mother liquor from the columns by dissolving in it more ammonia and pulverized sodium chloride and again carbonating the resulting solution to precipitate out more sodium bicarbonate, working at a lower temperature. Sodium bicar-

bonate is filtered off as usual and the mother liquor is strongly cooled to crystallize out ammonium chloride by the addition of further quantities of pulverized salt, and so on. The crystals are centrifuged, washed and dried at a low temperature.

The manufacture of ammonium chloride in conjunction with synthetic ammonia manufacture is an important feature in the modified Solvay process and will be dealt with fully in Chapter XXVII, "Modification and New Developments of Ammonia Soda Process."

Liquid Caustic. This is a strong caustic liquor from the evaporators of 48° to 50° Bé. containing 47 to 49 per cent NaOH. It is completely settled and clarified to separate out sodium chloride, sodium sulfate, and sodium carbonate. Liquid caustic is a comparatively new commodity, and is handled in rubber-lined railroad tank cars. Although the freight cost is higher (because of its water content), large consumers find it advantageous to receive liquid caustic in tank cars, as this minimizes the labor of handling. Liquid caustic is convenient to use and is cheaper than solid caustic because it does away with labor and fuel in dehydrating it to solid caustic. As the caustic freezes in winter, the tank cars must be provided with steam coils to thaw the content for unloading.

Flake Caustic. This is a solid caustic in thin pieces about $\frac{3}{8}$ inch by $\frac{1}{4}$ inch by $\frac{1}{32}$ inch thick. It is made by sending molten caustic to the flaking machine, in which a water-cooled drum rotates with the bottom segment immersed in the molten caustic. A thin film of caustic is picked up, solidified on the surface of the drum by cooling, and scraped off as the drum passes under a scraper. Flake caustic is favored by many consumers because of its ease of solution.

Powdered or Ground Caustic. These are forms of solid caustic that have been pulverized or ground in crushers to different degrees of fineness. The large surface area aids in solution.

Limestone and Limestone Products. At the quarries operated by most alkali plants, there are generally a number of strata of limestone of varying composition. Depending on the nature of these strata, the alkali plant operator markets limestone products as part of his business. Occasionally the strata must be separated to get the high quality kiln stone in the most economical manner. Such separation represents an appreciable part of the cost of quarry operation. Stone too high in silica, alumina, etc. is sold for cement manufacture, for road-building purposes, and as the coarse aggregate for concrete, and is occasionally finely pulverized and bagged as agricultural lime. Occasionally an alkali plant itself operates a cement plant from the waste mud of its caustic operation. It then quarries certain clay rocks selectively for the use as cement raw materials.

· **Liquid CO_2 and Dry Ice.** As has been pointed out in a number of places in this book, an ammonia soda plant has, as a general rule, an excess of carbon dioxide. This is over and above that available as boiler plant flue gases. Boiler flue gases from a specially constructed furnace which furnishes the raw material for most Dry Ice manufacture may run

between 12 to 16 per cent CO_2. The alkali plant has available varying quantities of gas ranging from a low of 23 per cent CO_2 (lime recovery rotary kiln gas) up to a maximum of 41 to 42 per cent (excess gas from a vertical lime kiln).

The gases from vertical and rotary kilns contain solid particles or dusts which must be separated out completely in order to avoid contamination of the absorbent. In ammonia soda plant practice this is commonly done with mechanical separators such as multiclones, etc. followed by a thorough water scrubbing.' For certain types of purification reagents, it is also important to separate out organics, particularly oxidizable impurities. This can be done with a potassium permanganate scrubbing tower.

The absorption medium requires occasional purification as in all Dry Ice processes. The peculiarities of the gas available in an ammonia soda plant are in no essential way different from those of any other Dry Ice operation. Hence they are not discussed here.

The ammonia soda manufacturers' principal reasons for producing solid and liquid CO_2 are twofold. First, they may have a large excess of relatively strong CO_2 gas available which gives them an advantage over other types of manufacture. Secondly, they may locate the plants where there is a fairly good market for either solid or liquid CO_2. Since the alkali manufacturers are very large coal consumers, the ammonia soda plants are located close to coal mines and thus have a potential market for CO_2 in the manufacture of mine explosives. CO_2 for explosive use is produced and shipped in liquid form. In small cylinders (up to 50 pounds net capacity) the liquid CO_2 is shipped at the atmospheric temperature which corresponds to an equilibrium pressure of about 1000 pounds per square inch. In large vessels, such as tank motor trucks and tank railroad cars, the common practice is to ship it at about 300 lbs. gauge pressure which corresponds to an equilibrium temperature of about 0° F. The tanks must therefore be very well insulated with low-temperature lagging. Liquid CO_2 explosive is particularly suitable for use in bituminous coal mines, which require a slow but progressive action in blasting, to obtain a large percentage of lumps.

Dry ice is extensively used in soda fountains, ice-cream chests, and meat refrigerators. It is also useful in fishing boats for preserving new hauls. It is, however, not so adaptable to the preservation of vegetables or fruits, as these plant products tend to ripen or rot rapidly in the atmosphere of CO_2 gas.

Chlorine and Chlorine Products. As will be seen in the following chapter, ammonia soda manufacturers have established electrolytic caustic plants themselves, making caustic soda, liquid chlorine, bleaching powder, and many chlorinated products. They are thus able to adjust the production of caustic soda between the lime process (causticization) and the electrolytic process in accordance with market demands. Because of increased uses of chlorine, the electrolytic production has made great strides in the last few years. Details of manufacture are given in Chap-

ter XX, "Manufacture of Electrolytic Caustic, Chlorine and Chlorine Products."

Sodium Nitrate. Ammonia soda manufacturers often establish and operate a nitrogen fixation plant for the manufacture of anhydrous ammonia by the direct synthesis of hydrogen and nitrogen gases. A portion of the ammonia may be oxidized to nitric acid which is then used in converting soda ash to sodium nitrate, selling this as nitrate of soda for fertilizer. It is in a much purer form than Chile saltpeter and is a better fertilizer than ammonium sulfate when used alone, because the latter leaves the soil acidic. Also the nitrogen in the nitrate form is more readily available to the plants.

Recently sodium nitrate was made directly from salt and concentrated nitric acid in the Solvay Process Company's plant (Hopewell, Virginia), yielding chlorine and sodium nitrate. Thus, chlorine is obtained without the joint product of caustic soda, or rather chlorine is obtained with its joint product in the form of sodium nitrate instead of caustic soda. This in time may constitute an important source for chlorine in conjunction with the nitrate manufacture from the oxidation of synthetic ammonia which can now be made so advantageously by ammonia soda manufacturers.

To complete the list may be mentioned by-products from distiller waste, such as calcium chloride (liquid, flake, or granulated), calcium sulfate, refined salt, soil lime, etc. Sometimes alkali manufacturers also make such products as sodium chromate and other sodium compounds, for which soda ash is used as a raw material. It is evidently impossible to include all the products manufactured by the ammonia soda manufacturers because of the many diversified products covered by various ramifications of the industry.

Chapter XVII

Position of Ammonia Soda Industry

The ammonia soda industry has played an important role in the fabric of the national industries. Not only in war but in peace does this industry form one of the most important pillars of the national industrial structure. The production of soda ash, like that of sulfuric acid, is an indicator of the industrial status of a country; however, unlike the sulfuric acid industry, the soda ash industry is controlled by a comparatively small group of people who supply the needs of the whole nation. This is also more or less true of other countries. Unlike the sulfuric acid industry, too, the ammonia soda industry is so far, for the most part, a closed one. Soda ash ranks next in importance to sulfuric acid. The acid and the alkali are the two most important basic chemicals a nation possesses, for, directly or indirectly, they are used as the raw materials for many other industries.

Having displaced the LeBlanc process, which was the sole process for soda ash manufacture for more than a century, the ammonia soda process has assumed a leading position. It is practically the only process by which the bulk of soda ash now is made. Like its predecessor, the LeBlanc soda industry, the ammonia soda industry forms a nucleus for many other industries. Besides the three main alkali products, namely, soda ash, caustic soda and sodium bicarbonate, many other products are made by ammonia soda manufacturers. The list of products has been described in detail in Chapters XV and XVI.

Recently the electrolytic caustic industry has been added to the ammonia soda constellation. It is a well known fact that chlorine, which is produced jointly with caustic soda in the electrolytic cells in the approximate ratio of 20 tons of chlorine to every 23 tons of the caustic, frequently sets a limit to the production of the electrolytic caustic industry. Formerly, the uses to which chlorine might be put were few, and the demand for chlorine was limited. It was the disposal of chlorine that formerly limited the output from the electrolytic industry; and the ammonia soda manufacturers had to adjust themselves between production by the chemical method and that by the electrolytic method. Today, the situation has entirely changed: the demand for chlorine has greatly increased and has, within the last decade, spurred the electrolytic production to such an extent that now the quantity of caustic soda produced by the electrolytic process as a joint product bids fair to exceed that produced by the lime (chemical) process.

Since 1926, six of the ammonia soda manufacturers have gone into the manufacture of electrolytic caustic. These are Solvay Process Co., Syra-

cuse, N. Y.; Diamond Alkali Co., Fairport, Ohio; Solvay Process Co., Baton Rouge, La.; Columbia Alkali Corp., Barberton, Ohio; Southern Alkali Corp., Corpus Christi, Texas; and Michigan Alkali Co., Wyandotte, Michigan. There are thus altogether seven such plants, including the Mathieson Alkali Works, Inc., with its separate plant at Niagara Falls, N. Y. Ammonia soda manufacturers are enviably situated for this enterprise because of the availability of cheap and abundant sources of brine and fuel. As will be mentioned in Chapter XX on the manufacture of electrolytic caustic, the two largest single items of cost entering into the manufacture of electrolytic caustic and chlorine are (1) salt (brine) and (2) power; the latter may now be generated very efficiently from coal by high-pressure turbo-generator plants. Mercury-arc rectifiers are now being used successfully in place of the dynamos or motor-generator sets for converting alternating into direct current, especially where the total voltage in the direct current circuit is high—at least 440v or more.

Also, the operation of an electrolytic plant gives ammonia manufacturers an extended range of products, such as liquid chlorine, bleaching powder, mono-chlorobenzene, para- and ortho-dichlorobenzene, synthetic hydrochloric acid and numerous other chlorine products, in addition to those discussed in Chapter XVI.

Table 103 shows these electrolytic plants owned and operated by the alkali manufacturers in the United States and their plant capacities as of 1940.

TABLE 103. Electrolytic Plants Operated by U. S. Ammonia Soda Manufacturers and Their Daily Capacities.

Plant	Location	Caustic Soda (short tons per day)	Chlorine (short tons per day)
Mathieson Alkali Works	Niagara Falls, N. Y.	119.3	106
Columbia Alkali Corp.	Barberton, O.	112.5	100
Diamond Alkali Co.	Fairport, O.	98	87
Solvay Process Co.	Syracuse, N. Y.	61 *	65
" " "	Baton Rouge, La.	47	42
" " "	Hopewell, Va.	(120) †	50
Michigan Alkali Co.	Wyandotte, Mich.	56.2	50
Southern Alkali Co.	Corpus Christi, Tex.	39.4	35

* Also 22 tons of caustic potash.
† As synthetic sodium nitrate.

Because of the demand for a pure grade of caustic for the rayon industry and others, liquid caustic of 50 or 70 per cent NaOH has been produced with a high degree of purity. As a result, there is a large increase in the production and shipment of liquid caustic by the ammonia soda manufacturers and a corresponding decrease in the fused caustic. On account of difficulty caused by freezing of the liquid caustic in winter, especially the 70 per cent grade, insulated and lined tank cars have been specially built. These retard solidification of the liquid caustic in cold weather, and also reduce contamination of the caustic by the container during shipment. For coastwise transportation, even a tank boat of con-

siderable capacity has been constructed for shipping a high grade liquid caustic in nickel-lined compartments somewhat similar to an oil tanker.

The ammonia soda manufacturers have long since identified themselves with the by-product coke industry They frequently supply coal gas to local cities. The incentive was evidently to secure a cheap source of ammonia supply in the form of crude ammonia liquor containing all the sulfides. Also, coke is required for burning limestone in soda manufacture. The gas, of course, can be used for power generation in alkali plants. The coke plant supplies ammonia and coke at low costs to the soda plants. Large alkali manufacturers generally run their own by-product coke ovens and the by-product coke industry has grown considerably with them. Among them may be mentioned such larger alkali manufacturers as the Solvay Process Co., Syracuse, N. Y.; the Michigan Alkali Company, Wyandotte, Michigan; and the Diamond Alkali Company, Fairport, Ohio. It is interesting to note that because of the need for ammonia in their process, the Solvay Process Co. was the first to introduce by-product coke ovens to America. The Semet-Solvay Co. had its origin in this and the plant was designed by Louis Semet of Solvay and Co. of Brussels. The situation is about the same with the European alkali manufacturers. For instance, the Imperial Chemical Industries, Ltd. (the former Brunner, Mond & Co., Ltd.), also operates, or controls the interest in, the by-product coke plants in England; and in fact a type of gas generator, called the Mond Gas Producer, was originally developed by Dr. Ludwig Mond, one of the chief founders of Brunner, Mond & Co., Ltd.

With the rise of the synthetic ammonia industry we find the ammonia soda manufacturers going into the manufacture of synthetic ammonia also, notably the Solvay Process Co., Syracuse, N. Y. (Allied Chemical & Dye Corp., Hopewell, Va.), and the Mathieson Alkali Works, Inc., Niagara Falls, N. Y. The raw materials for ammonia synthesis are hydrogen and nitrogen. Nitrogen gas in a concentrated form (95 per cent N_2 or more) is a waste product from tower washers in the ammonia soda process. Another good source of nitrogen and hydrogen is semi-water gas producers which use coke. Since ammonia soda manufacturers already operate by-product coke plants producing coke in quantities, they have an abundant supply of these raw materials. Further, they can use for the manufacture of ammonia soda the carbon dioxide gas washed from the water scrubber. Hydrogen gas may also be collected from cathode chambers of the electrolytic caustic cells operated by them. Moreover, nitrogen fixation plants need soda ash as one of the important raw materials for the production of synthetic sodium nitrate. For these reasons, the synthetic ammonia industry may well associate itself with the ammonia soda industry. Indeed, the Solvay Process Co. at Hopewell is the largest anhydrous ammonia producer of its kind in the United States.

It may be noted that with the advent of the synthetic ammonia industry there is a tendency to modify the orthodox Solvay process to permit the use of synthetic ammonia in the process for the simultaneous produc-

tion of ammonium chloride as fertilizer or as a chemical for dry battery manufacture. This undoubtedly has paved the way for the union of the ammonia soda industry with the synthetic ammonia industry.

As already pointed out, the recent market relationship between chlorine and caustic has been somewhat disturbed. Increased demand for chlorine has created a situation whereby increased output in caustic soda can find no new outlet. This situation is exactly the reverse of what existed in the early days of the alkali-chlorine industry. On this account, another process of obtaining chlorine without its counterpart in caustic soda production has attracted some attention. This was undoubtedly one of the stimuli that caused the Solvay Process Co. at Hopewell, Va., to perfect a process for obtaining sodium nitrate directly from salt. Prior to 1936, the plant at Hopewell had used exclusively soda ash from the Syracuse soda plant and nitric acid from the oxidation of the synthetic ammonia produced at the Hopewell plant, for the manufacture of sodium nitrate. When the price of sodium nitrate fell to the low level, it became necessary to substitute a cheaper raw material for soda ash for the manufacture of sodium nitrate. An old process therefore was revived and improved for the production of sodium nitrate directly by treating salt with nitric acid, obtaining liquid chlorine as a by-product. The reactions are

$$NaCl + HNO_3 \rightarrow HCl + NaNO_3$$
$$3HCl + HNO_3 \rightarrow Cl_2 + NOCl + 2H_2O$$
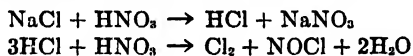
and the combined result is

$$3NaCl + 4HNO_3 \rightarrow 3NaNO_3 + Cl_2 + NOCl + 2H_2O$$

The nitrosyl chloride NOCl may be absorbed in sulfuric acid, forming nitrosyl sulfuric acid:

$$NOCl + H_2SO_4 \rightarrow SO_2.OH.ONO + HCl$$

or it may be absorbed in a ferric sulfate solution containing strong sulfuric acid. The nitrosyl sulfuric acid is then decomposed by steam and air into NO_2 and H_2SO_4, the latter being recovered, concentrated and used again. Absorption in sulfuric acid with the formation of nitrosyl sulfuric acid, however, has been abandoned because of the large quantities of sulfuric acid required and the cost of re-concentrating large volumes of dilute sulfuric acid. Briefly, the process may be described as one in which salt (NaCl) is treated with dilute nitric acid (about 70 per cent HNO_3) and the mixture heated in a reaction vessel. After most of the gaseous products have been driven off, boiling is continued and the steam evolved is led into a fresh reaction mixture that is being heated to the boiling temperature. This may be carried out in a series of reaction vessels or in bubble-cap columns. The gases coming out from the top consist of a mixture of NOCl, Cl_2 and H_2O and are treated with hot concentrated nitric acid (about 80 per cent HNO_3) in an oxidizing column for the oxidation of NOCl to Cl_2 and NO_2:

$$2NOCl + 4HNO_3 \rightarrow 6NO_2 + Cl_2 + 2H_2O$$
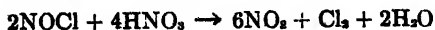
or are oxidized to NO_2 and Cl_2 by air in a reaction vessel using calcium aluminum silicate (zeolite) or aluminum oxide as a catalyst at a temperature of 300-400° C. and under a pressure of about 8 atmospheres.[*] The resulting gas mixture is then separated into its components NO_2 and Cl_2 in a rectifying column, where NO_2 (or N_2O_4) is cooled and condensed, and the free chlorine gas leaving at the top is liquefied to liquid chlorine in the usual way. The condensed NO_2 is then heated and oxidized to HNO_3 in an absorber with air under a pressure of 4-8 atmospheres, and the HNO_3 formed is absorbed in dilute nitric acid solution (40-60 per cent HNO_3) obtained from the nitrate evaporators, so as to enrich the acid to 70 per cent HNO_3 to be used again in the reaction vessels. From the bottom of the absorber, concentrated nitric acid (about 80 per cent HNO_3) is obtained, and this is used for the oxidation of NOCl in the oxidizing column described above.

The sodium nitrate solution from the reaction vessels contains excess of NaCl and some free HNO_3 which is neutralized with soda ash. The neutralized solution is at first concentrated under reduced pressure at a low temperature to separate sodium nitrate crystals and then under atmospheric pressure to remove NaCl. The crystals are filtered off and the mother liquor containing NaCl and $NaNO_3$ is returned to the process.

Some NO gas is always present in the gas as the decomposition product or combined with N_2O_4 as N_2O_3 which must be eventually oxidized back to nitric acid:

$$2NO + N_2O_4 \rightarrow 2N_2O_3$$
$$N_2O_3 + O_2 + H_2O \rightarrow 2HNO_3$$
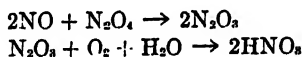
The process is a complicated one because of many side reactions which yield various lower oxides of nitrogen, and of the corrosive character of the large volumes of hot acids handled. The oxidation of NOCl for the separation of NO_2 from Cl_2 and absorption of NO_2 as strong HNO_3, leaving chlorine as liquid chlorine, are the essential steps involved in the process. The Allied Chemical & Dye Corp. have devoted several years time and heavy expenditure to perfect the process. A pilot plant was first erected, giving results that fully justified the construction of a commercial plant, producing 60 tons of sodium nitrate and 25 tons of chlorine per day. This plant was put in operation in 1936. It now produces 120 tons of sodium nitrate and 50 tons of chlorine per day.

Thus, a cheaper source of sodium has been used in place of soda ash for the manufacture of sodium nitrate, chlorine being produced as a valuable by-product. Such a production of chlorine without the accompaniment of caustic soda is bound to affect greatly the caustic-chlorine situation and will have important economic significance, now that a cheaper raw material than soda ash is used for the manufacture of the nitrate and a valuable by-product obtained in the form of liquid chlorine.

With the synthetic ammonia industry taken up by the ammonia soda

[*] Beekuis, H. A., U. S. Patents No. 2,138,016-7, Nov. (1938); No. 2,148,429, Feb. (1939); No. 2,150,669, Mar. (1939).

manufacturers, there are available considerable amounts of waste CO_2 gas from the water scrubber for soda manufacture, and certain quantities of waste ammonia gas purged off from the synthesis and purification system of the ammonia plant for use in replenishing ammonia loss in the soda plant. Further, with the abundant supply of free ammonia which must be fixed into some form of solid ammonium salt for fertilizer purposes, the ammonia soda process is bound to undergo certain modifications whereby ammonium chloride will be made more abundantly and cheaply for fertilizer than ever before. This will ultimately do away with the whole distiller operation and possibly also with lime kiln operation, if the synthetic ammonia manufacture and the ammonium soda production are geared in proper proportions.

A "Synthetic Sulfate of Soda" plant was established by Mathieson Alkali Works, Inc., at Lake Charles, La., for the manufacture of a substitute for salt cake used in kraft paper manufacture, by sintering soda ash with elemental sulfur in approximately molecular proportions, giving an equivalent of 96-97 per cent sodium sulfate. The manufacture is profitable and the product is taken by local paper mills, but it cannot compete with burkeite ($Na_2CO_3 . 2Na_2SO_4$), a double salt of sodium sulfate and carbonate, which is obtained as a by-product at the American Potash & Chemical Corp.'s plant at Trona, Calif.) shipped to the Gulf Coast from Los Angeles, Calif. One sample of the "Synthetic Sulfate of Soda" has the analysis given in Table 104.

TABLE 104. Composition of "Synthetic Sulfate of Soda." *

Na_2CO_3	74.53%
Sulfur	24.72
NaCl	0.13
Moisture	0.54
Other impurities	Undetermined

* Gillespie, W. F., "Operation of Sulfite Pulp Recovery Units on Soda Ash— Sulfur Mixture," *Paper Trade Jour.*, Technical Section, p. 36 (Dec. 26, 1940).

Thus it is seen that this is merely a fused block of soda ash and sulfur, having a potential sulfate content as in salt cake for kraft paper manufacture. It is a granular mass of greenish yellow color and is used as a make-up material for salt cake in the black liquor furnace, although the sulfur loss in the flue gases is somewhat higher.

Soda ash is consumed in large quantities by the glass industry which has developed simultaneously with the ammonia soda industry. The need of soda ash for glass manufacture is so great and so essential that it has been the practice with large glass manufacturers to operate their own soda ash plants. The Columbia Alkali Corp., for instance, is a subsidiary of the Pittsburgh Plate Glass Co., the Michigan Alkali Co. was started by the J. B. Ford Glass people (Capt. John B. Ford), and the Diamond Alkali Co. is privately owned by Evans Glass interests. This vertical combination between the raw material and the finished product manufacture as exemplified by the relation between the soda ash and

glass manufacturers is also common in other parts of the world. For example, in Japan, the Asahi Glass Co. owns and operates the Asahi Soda Co.'s plant located at Tobata, Japan. It is reasonable to predict that there may be a similar relationship between the caustic soda industry and the newly developed rayon industry. The historical relationship between the soap industry and the soda industry is too well known to be mentioned.

TABLE 105.   Estimated Distribution of Soda Ash in the United States.*

Consuming Industries	1929	1937	1939	1940 (estimated)
		Tons of 2000 lbs.		
Glass	672,000	903,000	820,000	904,000
Caustic and bicarbonate ⎱ Other chemicals ⎰	335,000	⎰751,000 ⎱650,000	810,000 600,000	780,000 710,000
Soap	213,000	180,000	190,000	182,000
Cleanser and modified sodas	125,000	140,000	130,000	135,000
Pulp and paper	110,000	104,000	105,000	111,000
Exports	40,000	55,000	80,000	61,000
Textiles	40,000	38,000	43,000	45,000
Water softeners	60,000	32,000	28,000	32,000
Petroleum refining	18,000	10,000	11,000	12,000
Miscellaneous	47,000	184,000	144,000	185,000
Total	1,660,000	3,047,000	2,961,000	3,157,000

* *Chem. Met. Eng.*, Jan. 1931; Feb. 1939; Feb. 1941; Biennial Census of Manufactures, Washington, D. C.

In Tables 105 and 106 are given the quantities of soda in one form or another consumed by different industries. From these data the relationship between the ammonia soda industry and the other industries will be evident.

TABLE 106.   Estimated Distribution of Caustic Soda in the United States.*

Consuming Industries	1929	1937	1939	1940 (estimated)
		Tons of 2000 lbs.		
Rayon and cellulose film	111,000	186,000	196,000	230,000
Chemicals	155,000	173,000	195,000	220,000
Exports	60,000	102,000	130,000	105,000
Soap	108,000	94,000	100,000	95,000
Petroleum refining	134,000	82,000	84,000	88,000
Pulp and paper	45,000	48,000	47,000	50,000
Lye	25,000	48,000	44,000	48,000
Textiles	42,000	45,000	44,000	48,000
Rubber reclaiming	40,000	17,000	18,000	20,000
Vegetable oils	11,000	20,000	17,000	16,000
Miscellaneous	48,000	173,000	150,000	175,000
Total	779,000	988,000	1,025,000	1,095,000

* *Chem. Met. Eng.*, Jan. 1931; Feb. 1939; Feb. 1941; Biennial Census of Manufactures, Washington, D. C.

Ammonia soda manufacturers have also become interested in cement manufacture in an attempt to utilize the lime sludge from the manufacture of chemical caustic and the abundant supply of high silica and high

alumina limestone unsuitable for soda manufacture. The lime sludge from the causticization of soda ash consists mainly of limestone ($CaCO_3$) with fine "sand" and a small excess of lime. If the caustic in the sludge is washed to below 2 per cent ($NaOH + Na_2CO_3$) on the dry weight, it does no harm to the cement product. At least two ammonia soda manufacturers in this country, the Michigan Alkali Co. and the Diamond Alkali Co., have operated or are affiliated with cement plants for this purpose. The latter produces several hundred barrels of cement a day in the same plant in which it manufactures its soda. The ammonia soda industry forms a good combination with the cement industry; for not only is the waste sludge from the manufacture of caustic utilized, but also the high-silica limestone, which is not suitable for lime burning in the shaft kiln, makes excellent raw material for cement manufacture. Cement so made helps carry the quarry costs.

In the ammonia soda industry, considerable "lean" carbon dioxide gas from the lime kilns cannot be used up in the manufacture of soda ash. This "lean" gas is a good deal richer in CO_2 than are flue gases from combustion of fuels. The carbon dioxide from such surplus gases may be absorbed in a series of two absorption towers using cooled potassium carbonate lye. It is then boiled off in a lye boiler. The liberated carbon dioxide is cooled, condensed, and compressed in a three-stage compressor to 1050 to 1070 lbs. per sq. inch. The compressed gas is again cooled in coils until it liquefies. It then is caused to freeze by expansion and the "pop-corn" snow is compressed into 10-inch cubical blocks weighing about 55 lbs. each. These compressed blocks are the so-called "Dry Ice." Often the gas is merely liquefied, placed in 50-lb. steel cylinders as liquid carbon dioxide, and sold to beverage and carbonated-water dealers. Substantial amounts of liquid CO_2 have been used in coal mining. For this purpose, it is supplied in a cartridge with a heater element which by its combustion furnishes enough heat to vaporize CO_2. The coal vein is thus loosened off by steady "push" and not by sharp explosion or detonation, with the result that a high percentage of lumps is obtained. Liquid CO_2 is also used in fire extinguishers.

TABLE 107. Annual Production of Liquid CO_2 and of Dry Ice
in the United States.*

Year	Liquid CO_2 (lbs.)	Dry Ice (lbs.)
1931	153,574,997	84,954,018
1933	117,382,256	59,057,600
1935	87,657,446	165,123,912
1937	100,715,662	313,217,310
1939	102,208,118	356,893,516

* Statistics of Bureau of Census, Washington, D. C.

Dry Ice is 141° F. lower in temperature than water ice and has about 10 times its refrigerating effect. Most of the Dry Ice production in 1940 (about two-thirds of the total made) was used in the ice-cream trade. Railroad refrigeration cars for transporting meat and frozen food, and

fishing boats also consumed considerable quantities. The annual production of liquid CO_2 and of solid CO_2 (Dry Ice) in the United States is given in Table 107.

Ammonia soda manufacturers have taken up this Dry Ice industry very actively. The Michigan Alkali plant at Wyandotte, Mich., has a daily capacity of some 200 tons of solid CO_2, while the Mathieson Alkali plant at Saltville Va., has about the same capacity. The fact that ammonia soda manufacturers have gone into high-pressure work, such as ammonia synthesis and liquid and solid CO_2 manufacture, is significant: it means that the industry is extending its ramifications, utilizing its available raw materials advantageously, and that it will assume a more important position in the national industries than heretofore. The industry has a group of chemically trained and mechanically experienced men well qualified for activities in new chemical fields.

Chapter XVIII

Manufacture of Refined Sodium Bicarbonate

Sodium bicarbonate, commercially known as baking soda or bicarbonate of soda, is a product directly related to the ammonia soda industry. Sodium bicarbonate in the crude state is first made in the carbonating towers or columns and filtered, and hence is also called "ammonia soda." From it soda ash is obtained by calcining. But this crude bicarbonate ($NaHCO_3$) from the filters contains as impurities sodium chloride (0.3 to 0.4 per cent NaCl on dry basis), ammonium bicarbonate (3.5 per cent NH_4HCO_3 on dry basis), a small percentage of ammonium chloride, and sometimes also traces of magnesium carbonate. Ammonium bicarbonate is decomposed in the dryers.

$$NH_4HCO_3 \rightarrow NH_3 + CO_2 + H_2O \text{ (steam)}$$
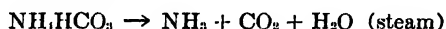
Ammonium chloride is converted to sodium chloride,

$$NH_4Cl + NaHCO_3 \rightarrow NaCl + NH_3 + CO_2 + H_2O \text{ (steam)}$$
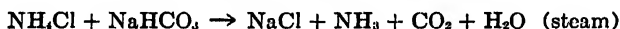
and the sodium chloride formed, together with sodium chloride present as such, is left in the soda ash. Any precipitate of magnesium carbonate in the bicarbonate will find its way to the soda ash which, when dissolved, shows turbidity in the solution. When the wet bicarbonate is dried by long exposure at a low temperature to prevent decomposition of sodium bicarbonate, it is difficult to decompose the ammonium bicarbonate completely and to drive off all ammonia from the sodium bicarbonate obtained. For, in a bicarbonate layer as thin as $\frac{1}{2}$ inch, dried at a temperature of 60 to 70° C. over steam coils for a period of 12 hours, enough ammonia remains in the dried bicarbonate to give a distinct odor, while about 10 per cent of the bicarbonate has been decomposed to normal carbonate. This is an unsatisfactory situation, to say nothing of the impurities left in the product obtained. Therefore pure sodium bicarbonate cannot be made directly this way.

At first thought it would seem natural to start with this crude bicarbonate from the filters and refine it. There are, indeed, many patents dealing with the refining of this bicarbonate by redissolving, recrystallization, etc. On account of the presence in it of 0.7 to 0.8 per cent total ammonia (as NH_3) which must be recovered, such methods cannot be carried out simply, and a step involving distillation of the bicarbonate solution is necessary if ammonia is to be saved. The ammonia soda manufacturers generally prefer to make it from soda ash. This seems to be a roundabout way, but after all it is simple and convenient from the manufacturing standpoint, because:

(1) there are no ammonia losses to contend with;

(2) carbon dioxide gas is recovered in a rich form from the dryers, while lean gas from lime kilns, which is usually in excess, may be used for recarbonating the sodium monocarbonate to bicarbonate;

(3) almost the same apparatus can be used in settling, carbonating, filtering, etc., as in soda ash manufacture. In fact, some of the antiquated apparatus from soda works is used in the manufacture.

On the other hand, there is a process employed by several alkali plants in this country, working from the crude bicarbonate by dissolving it hot, settling, distilling off ammonia, recarbonating the partially decomposed bicarbonate and filtering the precipitated bicarbonate. This process differs from the above only in the distillation operation, which would not be necessary when starting from soda ash. This process has merits, because ammonia may be saved and the CO_2 gas from the partial decomposition of the bicarbonate is recovered in a rich form by passing the exit gas through a condenser and cooler—to condense out steam—in much the same manner as in the distiller condenser or as in a furnace condenser system for handling CO_2 gases from the soda ash dryers. The same method has been used for the preparation of soda liquor for causticization from ammonia soda, except that the decomposition is carried somewhat further. (See Chapter XXI, "Wet Calcination of Sodium Bicarbonate.") Sesquicarbonate of soda ($Na_2CO_3 . NaHCO_3 . 2H_2O$) may be made from ammonia soda most advantageously in this way by decomposing (distilling) the bicarbonate to a proper degree of bicarbonation, cooling and crystallizing.

The process of manufacture of sodium bicarbonate from soda ash consists in dissolving soda ash to make a saturated solution, for which purpose a tank dissolver provided with a stirrer, or, better still, a rotary dissolver is used. The solution is settled in a series of vats (generally two or three); after cooling it flows by gravity to a large storage tank from which it is pumped to the bicarbonate tower, which is much the same as that used in soda ash manufacture but has less cooling surface. Cooling water is introduced at about 18 feet from the bottom of the tower. The gas employed is generally kiln gas and is introduced by carbon dioxide compressors as usual. The exit gas from the bicarbonate tower contains as high as 10 to 15 per cent CO_2. The draw temperature is higher (about 39° C.) than that in soda towers and the crystals are filtered and washed, first on a rotary drum filter, as in soda ash manufacture, and then in centrifuges much the same as those employed in the sugar refinery. Bicarbonate crystals from the filters here contain about 12-14 per cent water but are dried further in these centrifuges to a moisture content of about 8 per cent. Long cycle (as much as 8-10 min.) is used in these centrifuges in order to get dry product.

These centrifuges reduce the moisture left in the bicarbonate so as to enable it to dry more readily with less danger of decomposition. The filter liquor contains about 9 titer (*i.e.*, 9 cc. *N* acid per 20 cc. sample)

and is used over again in making soda solution. Thus, impurities such as sodium chloride, etc., are accumulated in the liquor. When this filter liquor gets too high in sodium chloride content through repeated use, it is sent to the soda ash plant for making saturated brine. Fresh water is then added for replenishment. When a bicarbonate tower gets "dirty" it must be cleaned; this is done by simply filling the tower with water and heating with steam. The boiled water is drawn out and after settling is stored in feed liquor tanks for making soda ash solution. No sulfide is introduced to the soda solution for carbonation in these bicarbonate towers.

In the study of equilibrium relationship of the Na_2CO_3-$NaHCO_3$-CO_2 system in water, Harte, Baker and Purcell [*] arrived at a useful empirical equation

$$\frac{x^2 C^{1.29}}{SP(1-x)(185-t)} = 10$$

where C = concentration of total Na in solution in equivalents per 1
    t = temperature of solution in ° C.
    S = solubility of CO_2 gas in water at temp. t under 1 atm. of CO_2 partial pressure
    P = partial pressure of CO_2 gas above the solution
    x = fraction of Na existing as $NaHCO_3$.

The relationship was established for a concentration (C) between 0.5 and 2.0 normals of Na, for partial pressures of CO_2 (P) within 1 atm. and for a temperature range from 20 to 70° C. While the investigation has not been extended to such a high partial pressure of CO_2 as exists at the bottom of the bicarbonate tower, this relationship undoubtedly holds good for a partial pressure considerably beyond 1 atm. With the concentration and temperature of the solution and the partial pressure of CO_2 above the solution given, the degree of bicarbonation (x) can be determined, because the solubility (S) of CO_2 in water under 1 atm. partial pressure is fixed by the temperature (t) in question. Values of S are as follows:

TABLE 108. Solubility of CO_2 in Water at 1 atm. Partial Pressure.

t (° C.)	S (Mol CO_2 per liter)
15	0.0455
25	0.0336
35	0.0262
45	0.0215
55	0.0175
63	0.0151
75	0.0120
85	0.0090
100	0.0065

This Na_2CO_3-$NaHCO_3$-CO_2 is a three-component system. In the Dry-Ice operation where absorption does not cause any sodium bicar-

[*] Harte, C. R., Baker, E. M., and Purcell, H. H., "Absorption of Carbon Dioxide in Sodium Carbonate-Bicarbonate Solutions," *Ind. Eng. Chem.*, **25**, 528 (1933).

bonate crystals to separate out, it has only two phases—solution and gas—and consequently it has three degrees of freedom. When, however, a solid phase separates out, as in the precipitation of $NaHCO_3$ in the bicarbonate tower, there remain only two degrees of freedom. The concentration of the solution then corresponds to a point of saturation which is a constant dependent upon the temperature only. This saturation point in the bicarbonate tower liquor is approximately 1.5 normal of total sodium in solution.

In the bicarbonate tower operation where the kiln gas (lean gas) containing 41 per cent CO_2 is pumped through the towers at a pressure of approximately 38 lbs. gage, and the draw temperature is around 35° C., it is possible to estimate the degree of bicarbonation in the soda solution at the tower draw. Here 38 lbs. gage pressure and 41 per cent CO_2 by volume correspond to 1.47 atm. partial pressure of CO_2 gas. Then

$$\frac{x^2(1.5)^{1.20}}{(0.0262)\,(1.47)\,(1-x)\,(185-35)} = 10$$

$$x = 98\% \text{ of total Na in solution.}$$
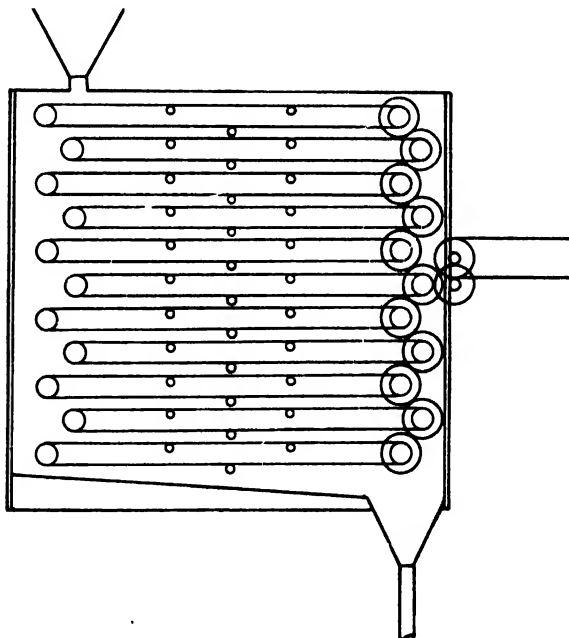
Fig. 72. Bicarbonate belt conveyor dryer.

The solid phase is then pure sodium bicarbonate. That is, at such a high partial pressure of CO_2 in the bicarbonate tower, the conversion of soda ash to sodium bicarbonate is practically complete. This is borne out in practice.

The bicarbonate from the centrifuges is dried, either on a continuous

belt conveyor consisting of a number of returned conveyor sections, all enclosed in a chamber with a steam stove at the entrance end to heat the incoming air and an exhaust fan at the other end to pull the hot air through and exhaust it to the atmosphere (Fig. 72) or, better still, as described below, in a vertical tube, about 50 feet high and 30 inches inside diameter (Fig. 73). The bicarbonate from the centrifuge is charged in through a feed table and is blown up by hot air, heated by steam stoves, from a centrifugal blower at the bottom of the tube. The bicarbonate particles suspended in the hot blast become dry as they reach the top, where two large cyclones in series are attached to the outlet of the tube to receive the dried bicarbonate. The exhaust from the second, and generally much larger, cyclone containing some extra-light particles, is led into a spacious dust-collecting chamber on its way to the atmosphere.
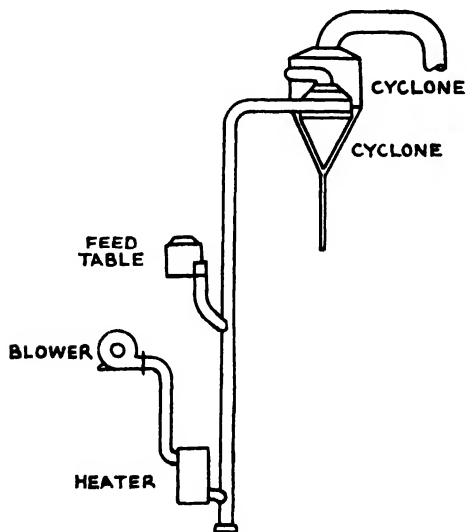
FIG. 73.

Bicarbonate d r y i n g tube.

This dust-collecting chamber is built of wooden frames, covered with cheesecloth. The temperature of the hot air is maintained at 70-90° C. and the blast from the centrifugal blower is at a pressure of 10 inches of water. A 30-inch tunnel, 50 feet high, of such a dryer will produce over 50 tons of dried bicarbonate per 24 hours. From the bottom of each cyclone, the bicarbonate is conveyed in a screw conveyor to packing bins, from which it is packed into wooden barrels weighing 400 pounds each or into small wooden kegs weighing 112 pounds each.

A slightly different arrangement is illustrated by Trump's Vertex Dryer (Fig. 74). The difference lies in placing the exhauster at the exit end of the second cyclone and in placing a larger cyclone collector directly next to the outlet of the dryer as a bin. The air at the inlet to the dryer is also heated to a higher temperature.

It might be interesting to follow the historical development of the manufacture of the pure bicarbonate of soda in the Solvay Syracuse plant. The manufacture of the refined bicarbonate of soda began in
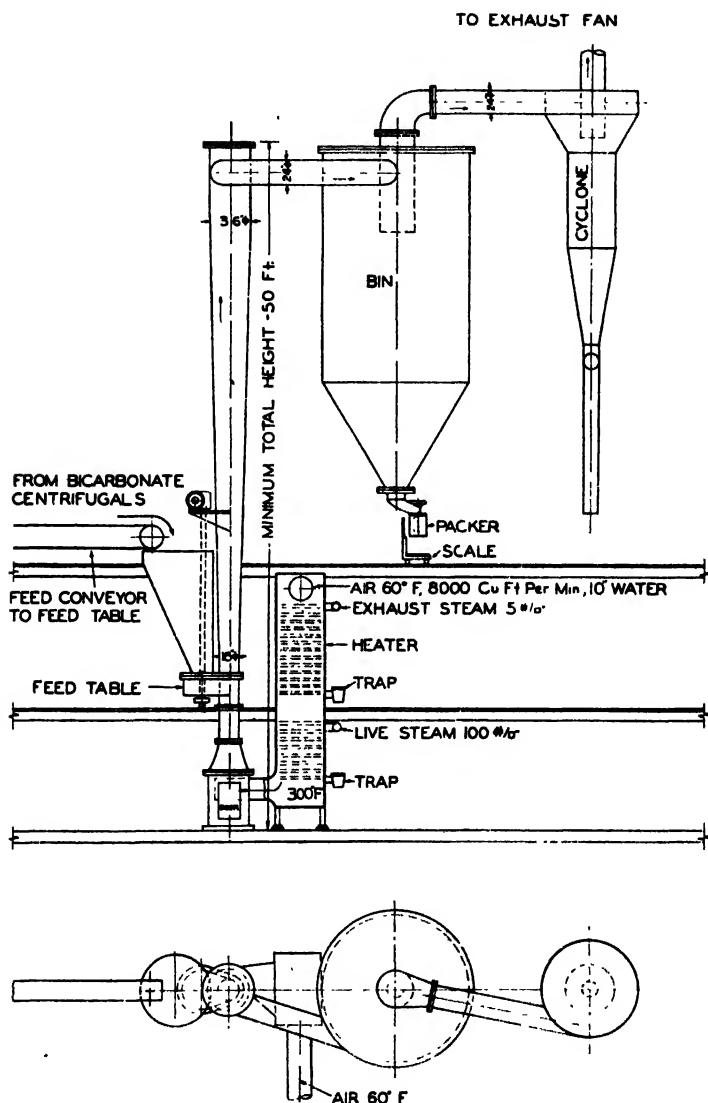
Fig. 74. Trump Vertex dryer.

Syracuse in October, 1887. The plant started with five tons of bicarbonate a day and gradually worked up to 300 tons a day. A plant has recently been added which may double this output.

For this purpose a solution of soda ash was made, settled, and recarbonated by sending lean gas (kiln gas) into a making tower. The crystals were centrifuged, and at the beginning were dried on trays using a low temperature. Then continuous belt conveyers were developed, consisting of eleven belt sections one on top of another, each section being about 50 feet long and 6 feet wide overall. These tiers of belt conveyors were housed in a casing with a fan blowing hot air at a temperature of 95° C. from one end to the other. The bicarbonate was fed onto the top belt by a roller and dropped from one belt to the other below (similar to that shown in Fig. 72) and was discharged from the bottom belt into a hopper. These dryers were doing 25 tons a day.

When more capacity was needed, through the inventive genius of Mr. Trump, a conical tube 24 inches diameter at the bottom and 48 inches at the top and about 50 feet high, with a feed table located near the bottom of the tube and an exhauster fan connected at the top of the cyclone, was built (see Fig. 74) and found to have a very large capacity. The air entered at the bottom and was heated in passing through a steam heater. At first it was thought that the temperature was limited to 95° C. but later it was found to be possible to increase it to as high as 150° C. in contact with the wet blanket, without driving off much CO_2. This was tested by putting an opening in the body of the tube, one at every five feet, and measuring the temperature of the bicarbonate at each point throughout the height. It was found that the temperature of the bicarbonate never got above 40-50° C. The exit air temperature is at 50° C. and the air velocity in the cone is about 600 feet per minute. The whole equipment extends to a height of more than 50 feet.

The volume of air required in this dryer varies from 8500 C.F.M. to 15,000 C.F.M. With a drop in air temperature of 100° C. (from 150 to 50° C.) the moisture evaporated may be 500 to 900 Kg. per hour. This gives a capacity of 150-270 tons of pure bicarbonate per day of 24 hours, when the bicarbonate from the centrifuges fed to the dryer contains 8 per cent moisture. The finished bicarbonate is fine and may be bolted for different meshes. A little dust may be saved by blowing the exit gases into bag filters or dust chambers as referred to above.

This type of dryer is also useful for drying other fine crystals, especially when they must be dried at a reduced temperature. Such materials may include ammonium bicarbonate, ammonium chloride, sesquicarbonate of soda, monohydrate of soda, etc. The dryer has a thermal efficiency of 70-75 per cent.

The bicarbonate so manufactured has a remarkably high degree of purity, as is shown in Table 109.

TABLE 109. Composition of Bicarbonate.

	Per Cent
$NaHCO_3$	99.80-99.92
$NaCl$	0.10- 0.20
Fe_2O_3	trace

This can be understood when we remember that it is made from ammonia soda which had, to start with, an exceedingly high purity of 99+ per cent Na_2CO_3 and 0.3-0.6 per cent NaCl. Students of Analytical Chemistry will understand why textbooks recommend the use of sodium bicarbonate as the starting point for preparing standard alkali and acid solutions for Quantitative Chemical Analysis. The alkali manufacturers undertake to manufacture it to meet the U.S.P. specifications directly.

Sodium bicarbonate is used for making baking powder, carbonated waters, beverages, in fire extinguishers, and in the manufacture of leather, drugs, and chemicals. It is also used in small quantities in stock food for the conditioning of hogs and cattle.

Chapter XIX

Manufacture of Caustic Soda—Chemical Process

Caustic soda is another important product manufactured by ammonia soda manufacturers. In many important industries, such as the soap, paper, mercerized cotton, viscose process for artificial silk, explosive, dyestuff, etc., alkali is employed in the form of the caustic and not the carbonate. The rayon industry is now one of the principal consumers of caustic. Ammonia soda manufacturers possessed some advantages for undertaking the manufacture of caustic. First, in conjunction with the manufacture of sodium bicarbonate which requires an excess of carbon dioxide gas from the lime kiln, the corresponding excess in lime obtained is best utilized in causticization; secondly, ammonia soda makes an extremely pure raw material for caustic manufacture, yielding a product at least comparable in purity with electrolytic caustic; and thirdly, unlike the electrolytic caustic industry, it has no joint product such as bleaching powder or chlorine to dispose of.*

Electrolytic caustic usually contains considerable amounts of sodium chloride, while the chemical caustic made from ammonia soda and good lime will yield a product of the degree of purity shown in Table 110.

TABLE 110. Purity of Chemical Caustic from Ammonia Soda.

	Per Cent
Na_2O	76.8
Na_2CO_3	0.6
NaCl	0.2

Further, the lime process has the advantage that salt (NaCl) present in the caustic soda made can be reduced to the amount corresponding to that present in the original soda ash used for causticization, by so controlling the process that all of the steam condensate (and little or no raw water) is used for the make-up (i.e., for washing the mud in the tail washer, for slaking the lime with the wash water, etc.). Electrolytic caustic is normally saturated with salt (NaCl) at the temperature of the strong liquor and at the concentration of NaOH in the strong liquor settlers. In the electrolytic process, calculated on a dry basis, the strong liquor made generally contains about 2 per cent NaCl and 98 per cent NaOH unless a special treatment is further applied (2 per cent NaCl being the amount corresponding to saturation in the strong liquor at the temperature and concentration in question); whereas in the lime process, NaCl per cent

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* At present, demand for chlorine has been very much increased and the production of electrolytic caustic has risen sharply.

can be maintained at as low as 0.2–0.3. This figure is far below the solubility of NaCl in the 48–50° Bé. liquor at the temperature of 25–35° C. and merely corresponds to the small amount of NaCl originally present in the ammonia soda used. For electrolytic caustic, therefore, good cooling and ample settling capacity must be provided to eliminate as much salt as possible from the strong liquor.

The method of causticization is well known:

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$$
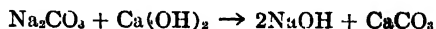
The reaction depends upon the low solubility product of Ca^{++} and CO_3^{--} ions causing the removal of solid $CaCO_3$ from solution. As both sodium carbonate and sodium hydroxide are very soluble, the reaction depends upon the relative solubility of calcium carbonate and calcium hydroxide in the solution in question. As the reaction proceeds, the concentration of sodium hydroxide increases. This increase, by common-ion effect, greatly decreases the solubility of calcium hydroxide until ultimately it is no more soluble than calcium carbonate, when the following equilibrium is set up:

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3$$
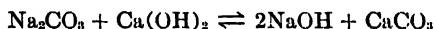
Thus conversion of Na_2CO_3 to NaOH cannot proceed to completion. Consequently at the end of the reaction in the resulting solution (lye), neither calcium hydroxide nor calcium carbonate can remain in solution to any large extent. That is to say, in the causticization reaction the equilibrium is reduced to that between sodium carbonate and sodium hydroxide in the resulting lye:

$$Na_2CO_3 + Ca(OH)_2 \text{ (solid)} \rightleftharpoons 2NaOH + CaCO_3 \text{ (solid)}$$
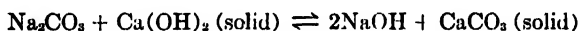
Therefore,

$$K = \frac{(2Na^+)^2 (2OH^-)^2}{(2Na^+)^2 (CO_3^=)} = \frac{(2OH^-)^2}{(CO_3^=)}$$

This equilibrium constant, K, is significant. For, to get high conversion (*i.e.*, to get OH^- concentration in the solution as high as possible and CO_3^- concentration as low as possible), the value of K must be as high as possible. Now in the resulting lye, since the concentrations of calcium hydroxide and calcium carbonate are small, we can assume complete ionization. So the solubility product of $Ca(OH)_2$ (K_1) will be $(Ca^{++}) \times (2OH^-)^2 = 4(OH^-)^3$, and that of $CaCO_3(K_2)$ will be $(Ca^{++}) \times (CO_3^=) = (CO_3^=)^2$. Therefore,

$$K = \frac{(2OH^-)^2}{(CO_3^=)} = \sqrt[3]{4K_1^2} \Big/ \sqrt{K_2} = 1.59 \left(\frac{K_1^{\frac{2}{3}}}{K_2^{\frac{1}{2}}} \right).$$

Therefore, K is a function of the solubilities of calcium hydroxide and calcium carbonate. From the mathematical expression we know that the smaller the constant K_2 and the larger the constant K_1, the larger K will be. In other words, *the more soluble the alkaline earth hydroxide, and the less soluble its carbonate, the more suitable it will be as a causticizing*

agent. This is a general principle governing the choice of a causticizing agent for the conversion of sodium carbonate to sodium hydroxide or of potassium carbonate to potassium hydroxide.

From the above expression

$$K = \frac{(2OH^-)^2}{(CO_3^=)}$$

where K is a constant at a given temperature, by dividing both sides by $(CO_3^=)$ and extracting the square root, we obtain

$$\frac{(2OH^-)}{(CO_3^=)} = \frac{K'}{\sqrt{(CO_3^=)}}.$$

where K' is the square root of K. Examining the mathematical expression of equilibrium, it may be seen that the more dilute the soda solution (*i.e.*, the smaller the concentration of $CO_3^=$), the higher will this conversion percentage be (*i.e.*, the ratio $OH^-/CO_3^=$ increases as $\sqrt{CO_3^=}$ decreases). With 10 per cent soda solution for instance, the theoretical conversion is 97 per cent, but in plant operation, using a 1.13 specific gravity liquor containing $12\frac{1}{2}$ per cent sodium carbonate, the conversion ratio is not over
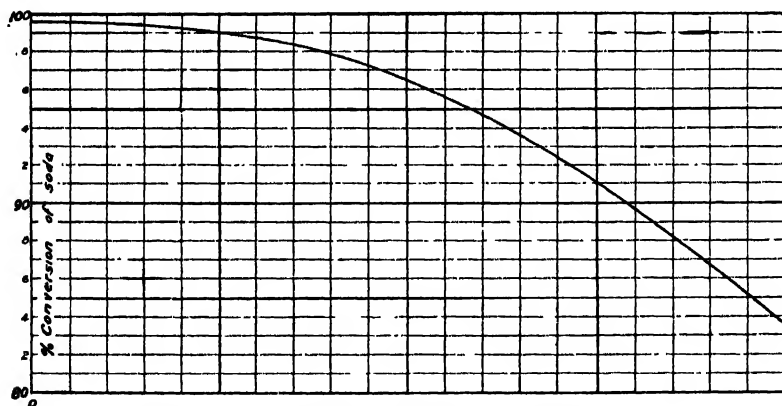
Initial per cent Na_2CO_3 (assuming dry slaked lime).

Fig. 75. The causticization equilibrium.

92 to $93\frac{1}{4}$ per cent. In practice it does not average much over 90 per cent conversion. Too dilute a liquor requires an excessive amount of fuel for concentration; hence a close study must be made between the degree of conversion obtainable and the cost of fuel for the concentration of the caustic lye. Fig. 75 shows the theoretical conversion curve giving the percentage of conversion from different concentrations of soda ash solution on the basis of using dry slaked lime.

Further, in the two reciprocal pairs: $Na_2CO_3 + Ca(OH)_2$ and $CaCO_3 + 2NaOH$, there are four components—any three of the above four compounds with water as the fourth component. There are therefore two

degrees of freedom (temperature and pressure). At a given temperature and under a given total pressure, there are all together only four phases —two solid phases, a solution, and a vapor phase. Normally $Ca(OH)_2$ and $CaCO_3$ in the sludge are the two solid phases in question, but nothing can prevent the formation of a double salt in place of one of the two solid phases. In fact, such a double salt as Pirsonnite ($Na_2CO_3 . CaCO_3 . 2H_2O$) or Gaylussite ($Na_2CO_3 . CaCO_3 . 5H_2O$) has been found in the sludge from the more concentrated soda solutions, especially at low temperatures. This would lead to greater losses of soda when too great a soda concentration is employed.

It may not be out of place to point out here that the temperature does not influence the degree of conversion to any great extent. This means that the temperature coefficient in van't Hoff's equation of chemical equilibrium: $\dfrac{d \ln K}{dT} = \dfrac{-Q}{RT^2}$ is small; *i.e.*, $-Q$, the heat of causticization, is small. In practice, so long as the temperature is high enough to bring about the reaction quickly and to get a rapid settling for the sludge, the temperature of causticization is rather immaterial. This may not be the case if a causticizing agent other than lime is used. For instance, if strontium oxide is used instead of lime, the heat of causticization is positive and large, and a higher temperature would yield a lower conversion.

The following description applies to a small caustic plant. The soda solution from storage tanks which is made up at the specific gravity of 1.13 (17° Bé.) is causticized in large tanks, 10 to 14 feet in diameter, 8 to 9 feet deep with a flat bottom. Steam is used to heat the liquor to 185 to 195° F. and a compressed air line may be provided for agitating. The tanks are each provided with a mechanical stirrer having a set of bevel gears driven by a pulley from a counter-shaft. Lime in lumps of 6-inch size or smaller is added to a steel basket attached to the side and partially submerged in the liquor, in an approximate ratio of 60 pounds lime to every 100 pounds of sodium carbonate in solution. The exact amount of lime depends upon the quality of the lime and the amount of excess desired. The bottom and sides of the basket are perforated with ½-inch holes. When closer control is desired, instead of solid lumps, milk of lime having a concentration not less than 250 grams of CaO per liter is used. Several of such tanks can be used in rotation, one being in operation while the others are settling and washing. Decantation of the supernatant caustic solution is performed through a swing pipe with outlet nozzle attached to the side near the bottom of the tank.

After sufficient lime has been added and the desired conversion percentage obtained as shown by titration with "double indicators," the liquor is allowed to settle for about 2 hours. The clear portion is drawn off through the swing pipe. This gives a 14½° Bé. lye containing about 10 per cent sodium hydroxide. The lime sludge, with whatever lye remains, is washed with the third liquor from a previous batch, the stirrer is started, and the liquor heated with steam. After settling, this gives the second liquor of 7 to 8° Bé. that may be added to the lye tank. This

slime is again washed with the fourth liquor in a similar way; this gives the third liquor which is used for the second washing and also for making soda solution for causticization. Finally, the slime is further washed with fresh water, giving the fourth liquor. This washed slime containing the precipitate of calcium carbonate with a little alkali that remains, is washed out and sent to waste. A batch of causticization can be made in every $2\frac{1}{2}$ to 3 hours; but this, coupled with the time for washing, settling and decanting, makes the cycle for each tank about 16 hours. This washing process is a very important one, although slow and tedious; considerable soda could be lost through careless washing. Sodium carbonate seems to be held quite tenaciously by the slime, supposedly as a double salt formation with calcium carbonate in solid form.

A more modern practice that gives more thorough washing with a smaller quantity of water and a stronger caustic lye is to use the Dorr system of continuous causticizing agitators and thickeners.

The following is a description of a large causticizing plant using the Dorr agitators, thickeners, lime slaker, classifier, rotary filters, diaphragm pumps, and rotary lime kiln.

Strong soda solution of about 18-20 per cent sodium carbonate is made in a rotary dissolver using the weak wash liquor for solution. Lime is slaked to a dry hydrate in a rotary lime slaker using also the weak wash liquor. The hydrated lime coming from the slaker is then suspended in larger quantities of the weak wash liquor to form a strong milk of lime containing about 250 grams of CaO per liter. The milk of lime passes through a mechanical "classifier" in which the unburnt stone, the finely divided overburnt lime, and sand are separated, yielding a rather pure lime suspension. The soda solution is first causticized with a large excess of lime in the primary causticizing agitators, generally three in a series, from the last of which the lye suspension is then settled in large continuous thickeners. The overflow clear lye from the first thickener furnishes the strong caustic for evaporation. The sludge from the bottom of the first thickener is pumped out by means of a diaphragm pump to a rotary drum filter (generally of the Oliver type), from which the cake containing an excess of free lime is further treated with about 10 per cent excess of weak soda solution in a secondary causticizing agitator. The filter liquor from this filter is returned to the first thickener. From the secondary agitator the lye suspension is settled in the second thickener, the overflow from which furnishes the weak wash liquor for making soda solution in the dissolver and for hydrating the lime and making milk of lime in the lime slaker and "classifier." The sludge from the second thickener is pumped to the third thickener, in which fresh water is introduced for the final washing and from which the sludge is pumped to another rotary drum filter. Fresh water also is used on this filter to wash the cake and the filter water is returned to the third thickener. In this way, the recovery of alkali is as high as 99.7 per cent. The upkeep is low, the power consumption quite reasonable, and the floor space required comparatively small.

Instead of using milk of lime and soda solution, it is also feasible to introduce solid soda ash (ammonia ash) into milk of lime in a mixing trough together with some wash liquor. Soda ash is introduced by means of an adjustable pusher driven by a worm gear and is dissolved in the milk of lime in the mixing trough. About 90 per cent of the causticization work then takes place in this mixing trough, from which the suspension overflows to the bottom of the causticizer in which the liquor is heated by steam coils. From the top of the causticizer, the suspension in which the chemical reaction is practically completed overflows to the settlers or thickeners.
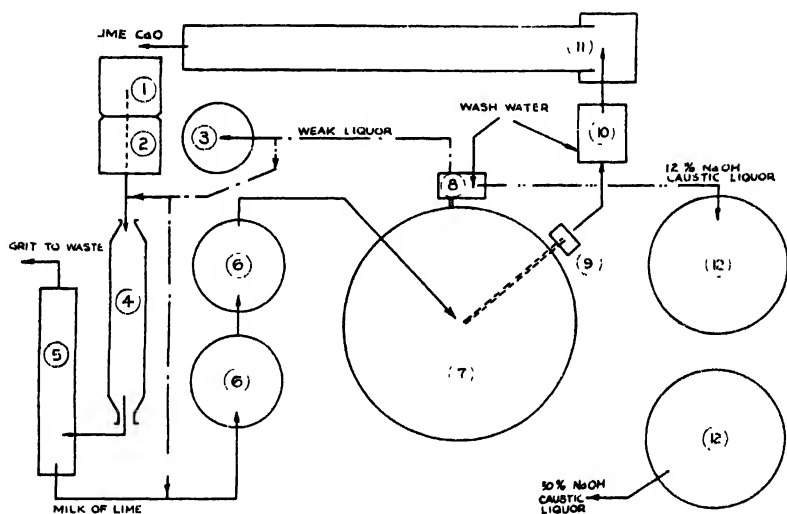
FIG. 76. A small caustic plant with lime recovery.

1. Reburnt Lime Storage
2. Fresh Lime Storage for Make-up
3. Weak Wash Liquor
4. Rotary Lime Slaker
5. Dorr Classifier
6. Causticizers (two units)
7. Dorr Multi-compartment Tray Thickener
8. Caustic Liquor Overflow
9. Diaphragm Type Sludge Pump
10. Rotary Vacuum Filter
11. Lime Reburning Rotary Kiln
12. Double Effect Caustic Evaporators

The mud from the last filter is either reburnt in a rotary kiln or sent to waste. Rotary lime kilns are suitable for burning the fines like the caustic mud. Too much caustic left in the mud may cause attack of the refractory lining of the rotary kiln, necessitating frequent renewal and interruption of operation. This caustic mud is nowadays sometimes utilized in cement plants operated in connection with the ammonia soda industry. If the alkali content is kept below 2 per cent on the weight of the dried cake, it does no harm for cement manufacture. If a good quality of limestone is available, and if the milk of lime has been purified in the "classifiers," the caustic mud obtained in this way can be used for the manufacture of whiting.

A very compact arrangement representing a practice slightly different from the above is illustrated in a small modern caustic plant (15-20 ton capacity) using 23° Bé. soda solution (18 per cent Na_2CO_3) for causticization and causticizing it with concentrated milk of lime (250 g CaO/l) to obtain 12 per cent caustic liquor. This has the arrangement represented diagrammatically in Fig. 76.

In this plant the caustic sludge is reburnt in a rotary kiln (11) and the reburnt lime is stored in a bin (1) next to a fresh lime bin (2). The lime is fed into a rotary slaker (4) by means of a mechanical feeder (apron type conveyor) and slaked with water containing weak liquors from wash water. Then the milk of lime goes to a Dorr classifier (5) for removing unburnt stone or deadburnt lime. This concentrated milk of lime together with some weak liquor is sent to causticizers (6)—two in series in which a turbine type agitator is used—and the effluent goes to a Dorr washing tray thickener (7) in which there are three compartments for counter-current washing. The washed sludge is pumped by means of a diaphragm pump (9) and filtered on a rotary vacuum filter (10), on which the cake is further washed with fresh water and then sent to the rotary kiln (11) for reburning. The wash water is utilized for slaking lime in the rotary slaker and stored in storage (3), but the stronger wash liquor may be added to the milk of lime for causticization. The clear caustic liquor (12 per cent NaOH) overflowing from the washing tray thickener is sent to double effect evaporators for concentrating to 47°-49° Bé. liquid caustic. Here a multi-compartment thickener is used instead of a series of three individual thickeners, as mentioned above, to save floor space. Lime recovery is effected by burning the sludge in a rotary kiln. A small amount of fresh lime is required for the make-up.

As has been noted above, the washing of the caustic sludge is a most tedious job. The success of this chemical process of caustic manufacture, therefore, depends largely on the efficiency of the washing operation both to cut down the loss of alkali and to keep the volume of the liquor as small and the caustic as concentrated as possible. Without an efficient means of washing, both of these requirements would be impossible of fulfillment. It can be readily understood that the rate of settling of the suspended lime sludge in the caustic liquor has a great influence on the washing of the sludge by the process of decantation either in settling tanks or in the Dorr continuous thickeners. A great deal of study has been made of the conditions and ways and means whereby a high rate of settling, *i.e.*, of separation of the solids from the liquid phase, can be secured. It has been found that the coarser the solid particles held in suspension, the higher the temperature of the solution during causticization (within certain limits), and the more dilute the lye, the better is the settling rate for the solids from the liquid phase and the more complete is the separation. In washing the caustic sludge, the purpose is to separate the soluble alkali as much as possible from the solid lime sludge held in suspension; and the rate of settling of the suspended solids from the wash liquor has a direct bearing on the ease of washing. In the first place,

lime, if first slaked in the weak caustic liquor to form a dry hydrate and later re-pulped in a desired quantity of that liquor to form the milk of lime, aids the rate of settling.* In the second place, long and violent agitation in the causticizing agitators, or high peripheral speed at which the stirrer is driven, impedes the rate of settling. It has been pointed out that a high concentration of the soda solution results in a low conversion of the caustic. By using a strong soda solution in the so-called primary causticizing agitators and a large excess of lime, a strong liquor coupled with a high conversion is thus secured, the excess lime in the sludge being later treated with more soda solution in a secondary causticizing agitator. To aid the separation of the liquid from the solids, a rotary filter is employed, so that the caustic solution may be more completely separated from the solid sludge. As it is theoretically impossible with a finite number of washings to wash out all the alkali from the sludge, considerable alkali remains in the sludge in the form of a liquid retained in the solid particles. The moisture in the sludge from free settling in the thickeners is generally as much as three times the weight of the dry solid particles. If the moisture content in the mud can be cut down it is evident that the loss of alkali in the washed mud will be greatly reduced. Hence to minimize the loss of alkali in the caustic mud, the sludge leaving the third thickener is pumped to another rotary filter and the mud cake washed on the filter with fresh water. Thus, the loss of the alkali is cut down to 0.3 per cent, giving a recovery of 99.7 per cent. The efficiency of the Dorr system lies in (1) the efficient separation of the solids from the liquid phase leaving the solids in a compact form of sludge, and (2) in the strictly countercurrent arrangement whereby the sludge is washed as it passes through each stage. A filter inserted between the primary and secondary causticizing agitators serves to remove the strong caustic lye from the sludge containing excess lime, to be further treated with fresh but rather dilute soda solution in the secondary causticizing agitator. The final filter at the end of the system which handles mud from the third thickener greatly reduces the amount of the alkali-bearing water in the mud, thus minimizing the loss of alkali from the system. It was found also that with a moderate rate of stirring during causticization and employing not too long a duration for stirring, so long as the temperature is maintained above 85° C. (or 185° F.), a favorable rate of settling can be secured. A good grade of lime (*i.e.*, high CaO lime) also gives better rate of settling than a poor grade.†

The lye from the strong liquor storage tanks is concentrated in multiple-effect vacuum evaporators, having generally two of these effects. The commonest types of these evaporators are the Zaremba, the Scott, the Swenson, and the Kestner, using exhaust steam. Because of the elevation of boiling points as the caustic liquors become more and more con-

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* W. E. Piper, "Recent Advances in Causticizing Theory and Practice," *Trans. Am. Inst. Chem. Eng.*, 1930.

† J. Harrop and H. O. Forrest, "Causticization of Soda Ash," *Ind. Eng. Chem.*, April, 1923.

centrated, the temperature difference between the steam side and the liquor side in each effect is limited, and it is generally impractical to use more than three effects in the evaporator system using exhaust steam. These evaporator tubes are made of steel or copper ($2\frac{1}{2}$ inches outside diameter and about 6 feet long) but for manufacturing caustic for the rayon industry, the use of copper is objectionable. Steel tubes are almost as good as nickel up to 50 per cent, but above this concentration pure nickel tubes are superior. Where steel tubes are used, the effect of embrittlement of the thin steel tubing by the action of strong caustic makes it rather unsafe to use steam of higher pressure than exhaust steam. The use of a high-pressure steam (say 125 pounds per square inch) is, however, made possible by the introduction of pure nickel tubes. Ordinarily, the caustic liquor from the last effect is concentrated up to 46° to 49° Bé., corresponding to a point of minimum freezing temperature in the freezing point curve for caustic solutions within this range. This hot strong caustic is drawn out into tall, cast-iron tanks in which salt (NaCl) and soda (Na_2CO_3) separate out at the bottom, these two salts being only sparingly soluble in the caustic solution at this concentration. Separation of these two salts from the caustic is aided by cooling; but if it is allowed to cool too far, the caustic becomes so viscous that the rate of settling may be retarded and considerable sodium hydroxide crystals may separate out together with the salt and soda crystals at the bottom of the settling tanks. One analysis of this concentrated caustic hydrate sediment (from liquor of 1.50 sp. gr. at 15° C.) is given in Table 111.

TABLE 111. Composition of Strong Caustic Sediment.

	Per Cent
NaOH	41.56
NaCl	8.50
Na_2CO_3	4.17
Na_2SO_4	1.70
Fe_2O_3	1.36
H_2O and undetermined (by difference)	42.71

The composition of 48° Bé. caustic is approximately as follows:

TABLE 112. Composition of 48° Bé. Caustic.

NaOH	690	grams per liter
Na_2CO_3	2	" " "
Na_2SO_4	4	" " "
NaCl	2	" " "

It is necessary to bring the caustic liquor in the multiple-effect evaporators to 47° to 49° Bé. so that on settling and cooling both sodium carbonate and sodium chloride may settle out, yielding a high-grade caustic for fusion; for these two salts become sparingly soluble at this concentration. Even then, if these two salts are present in quantities up to their respective saturation points (NaCl in the electrolytic method and Na_2CO_3 in the lime process), there could be approximately 1.0 per cent

NaCl and 0.5 per cent Na₂CO₃ remaining completely dissolved in a 50 per cent NaOH liquor at 30° C. Therefore, the best way is to keep out these two salts as far as possible. If, for some reason, these two salts have not been eliminated from the caustic liquor, it would be impossible to expect a high-grade caustic from the pots. For good caustic can come only from a well-settled, properly concentrated liquor. A sample of solid caustic obtained from a well-settled but insufficiently concentrated caustic liquor (38° Bé.) gave the following analysis:

TABLE 113. Composition of Solid Caustic Obtained from
Insufficiently Concentrated Liquor (38° Bé.).

	Per Cent
NaOH	93.54
Na₂CO₃	4.17
NaCl	1.28
Na₂SO₄	0.99

It will be seen that if the caustic liquor from the evaporators was not up to normal strength for settling, many of these impurities would remain dissolved and would not settle out.

The clarified 46° to 49° Bé. solution can be drawn to a number of cast iron, open-fusion pots, generally direct-fired with natural gas, oil, or coal. Sometimes hydrogen gas from the cell room is burnt under these pots, in which case a pilot gas pipe must be provided burning natural gas or coal gas all the time to prevent accident of explosion caused by the hydrogen flame being extinguished, leaving an explosive mixture in the furnace. As these heavy, cast-iron, direct-fired pots are very inefficient in the utilization of heat, attempts have been made to substitute evaporators for the pots at least during the earlier part of the pot fusion work. With a single-effect, nickel-tube evaporator, using 125 pounds per square inch of steam, it is feasible to concentrate further the caustic by means of evaporators from 48° Bé. to as high as 75 per cent NaOH concentration using forced circulation. A few alkali plants have already adopted this procedure.

The cast-iron fusion pot above referred to is approximately 10 feet inside diameter and 6 feet 3 inches deep, the shell of the pot being about 3 inches thick at the bottom. Each pot of this dimension will hold 19 tons of finished solid caustic. Some caustic pots in use are much larger than these, but these are considered to be the standard size now. (On the other hand, some pots are only 6 feet in diameter by 4 feet 6 inches deep, holding 10 to 11 tons of finished caustic per batch.) These pots are frequently arranged in two rows. The back pots, placed 12 inches higher than the front ones, are for preliminary concentration, while the front one are used for the final concentration. Strong caustic liquor enters the back pots and receives preliminary concentration before it is transferred to the front pots, where more intense heating occurs. This arrangement gives a countercurrent gradation in firing and avoids the inconvenience experienced when adding weaker caustic liquor to a pot containing nearly

completely dehydrated molten caustic. It also shortens the working cycle for the final pots and prolongs their life. The pots are made of dense gray iron, preferably with some nickel added (1 to 1½ per cent nickel) to make the composition more resistant. The greatest skill is required in casting them. In their settling, these pots should be supported at the bottom rather than suspended from the top flanges (Fig. 77). Local over-heating is very serious and should be guarded against, especially near the bottom of the pot toward the fire. The flame usually comes in near one
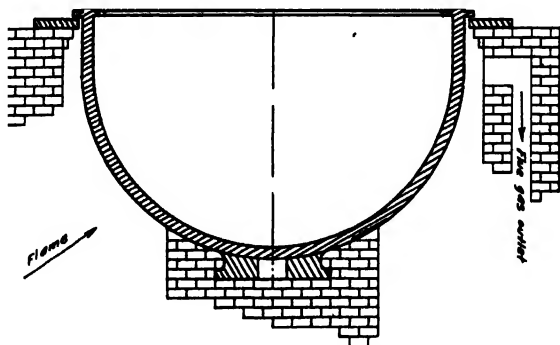
Fig. 77. Caustic pot as installed.

side of the furnace wall, is caused to surround the pot, and leaves by the other side of the furnace on its way to the stack; a narrow partition wall divides the front into two halves. For this reason it is recommended that these pots be turned around 60° or 90° after about every 15 heats. With proper care in maintenance a fusion pot should last for about 200 heats.

When the 48° Bé. caustic is charged to the back pots, the liquor at first boils violently, but soon the ebullition subsides although the temperature steadily rises. Pungent odors are noticed. When it has been concentrated in these back pots for from 24 to 48 hours depending upon the size of the charge and the method of firing, it is transferred to the front pots continuously and raised to a strong heat. Finally small bubbles come up flickering through the quiet molten mass. The temperature here will have reached 500° C. (as shown by the incipient fusion of anhydrous cupric chloride contained in a thin iron tube immersed in the molten caustic.)* After an hour or more, the fire should be gradually withdrawn and the pots allowed to settle until a temperature of about 350° C. is reached.

In settling, most of the sodium carbonate in the molten mass separates out, but little sodium chloride is thrown down at this final stage. Prac-

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* A recording pyrometer is now regularly installed to register the temperature cycle in the pot.

tically all the iron oxide, however, should have settled to the bottom. The end point of fusion can easily be judged by the behavior of the molten mass in the final pots and by examining the texture of a sample of solidified caustic obtained. The time required for cooling and settling is from 16 to 24 hours, making a complete cycle of operation from 3 to 4 days. The color of the caustic obtained sometimes is found to be dark green, sometimes slightly reddish. The former condition is caused by the incomplete oxidation of iron and other impurities, due to too low a temperature in the final pots; the latter is due to insufficient settling. Proper fusion followed by a quiet settling is a *sine qua non* for a colorless, high-grade product. The presence of manganese in the form of Na_2MnO_4 causes a dirty green color, in which case a little flowers of sulfur should be thrown over the surface as it cools, but before it is cooled to 400° C. Too much sulfur in the caustic imparts a yellow-red tinge due to the formation of fused sodium sulfide. Normally 5 to 15 lbs. of sulfur are added to each pot. If fusion is carried out properly and the molten mass given proper settling, nothing need be added to obtain a good color and a proper product, but generally the sulfur treatment is desirable. When the content of a final pot has been allowed to settle and cool to about 350° C., the molten mass is ladled, or better, pumped out by an air-driven vertical centrifugal nickel pump, into drums made from No. 22-gage steel plates. Each drum contains 700 pounds net of solid caustic. The mass solidifies on cooling with a conical depression at the center and the drum is immediately sealed to prevent absorption of moisture. This is the commercial 76 per cent (Na_2O) caustic containing over 98 per cent sodium hydroxide. The specific gravity of the solid caustic varies somewhat but is almost 2.0. The chemical analysis of a good "76" caustic is given in Table 114.

TABLE 114. Analysis of Solid Caustic.

	Per Cent
NaOH	98.70
Na_2CO_3	0.60
NaCl	0.30
Na_2SO_4	0.20
Water and undetermined substances (by diff.)	0.20

When the strong caustic liquor for some reasons contains large amounts of iron, a dark scum appears on the surface of the caustic at the beginning of concentration in the back spots. The scum is found to have the composition given in Table 115.

TABLE 115. Composition of Scum.

	Per Cent
Insoluble matter (in water)	3.64
Insoluble matter (in acid HCl)	trace
Fe_2O_3	3.52
NaOH	29.86
Na_2CO_3	18.42
NaCl	1.52
Water and undetermined substances (by diff.)	46.68

Unlike the LeBlanc black liquor, there is no sulfide or thiosulfate in the ammonia soda and no niter need be added. But good settling is very essential. That portion of molten caustic left at the bottom after settling, known as the caustic "bottoms," is of reddish-brown color and contains considerable ferric oxide and sodium carbonate and some sodium chloride. One analysis of such a sample is given in Table 116.

TABLE 116. Composition of Caustic Bottoms.

	Per Cent
NaOH	85.12
Na$_2$CO$_3$	6.27
NaCl	2.25
Fe$_2$O$_3$	4.67
Impurities undetermined (by diff.)	1.59

When there is a ready market, the caustic bottoms are sold as such; otherwise it is dissolved to make a 48° liquor and the iron then separated by decantation.

In Table 117 is a temperature record for an experimental (1¼ ton) fusion pot whose cycle of operation was about 42 hours.

TABLE 117. Temperature vs. Time Record During Fusion Operation.
(Caustic liquor sp. gr. 1.470 at 23° C.)

No. of Reading	Time	Temp. of Caustic in Pot (° C.)	No. of Reading	Time	Temp. of Caustic in Pot (° C.)
1	3:30 A.M.	130	17	7:30 P.M.	188
2	4:30 A M.	133	18	8:30 P.M.	198
3	5:30 A.M.	140	19	9:30 P.M.	208
4	6:30 A.M.	142	20	10:30 P.M.	220
5	7:30 A.M.	145	21	11:30 P.M.	235
6	8:30 A.M.	154	22	12:30 A.M.	275
7	9:30 A.M.	156	23	1:30 A.M.	288
8	10:30 A.M.	...	24	2:30 A.M.	...
9	11:30 A.M.	158	25	3:30 A.M.	300
10	12:30 P.M.	166	26	4:30 A.M.	311
11	1:30 P.M.	172	27	5:30 A.M.	320
12	2:30 P.M.	...	28	6:30 A.M.	340
13	3:30 P.M.	179	29	7:30 A.M.	360
14	4:30 P.M.	...	30	8:00 A.M.	445 *
15	5:30 P.M.	184	31	8:30 A.M.	498 †
16	6:30 P.M.	185			

* Tested by b.p. of sulfur.
† Tested by the m.p. of CuCl$_2$.

It will be noticed that at the beginning the temperature of the caustic rises only slowly, but toward the end when the specific heat of the more or less completely dehydrated caustic decreases, it rises rapidly. The trend of the curve in Fig. 78 shows this.

In Table 118 is given a temperature record of a 19-ton coal-fired caustic pot whose cycle of operation was about 72 hours. Chemical (lime) caustic of 50° Bé. was concentrated in these pots and the tempera-

tures were recorded by an alumel-chromel pyrometer with a compensated cold end. A long C. I. tube is used for the protection of the pyrometer bulb. The pot was fired rather slowly and the highest temperature of the molten mass did not attain quite the usual normal peak.
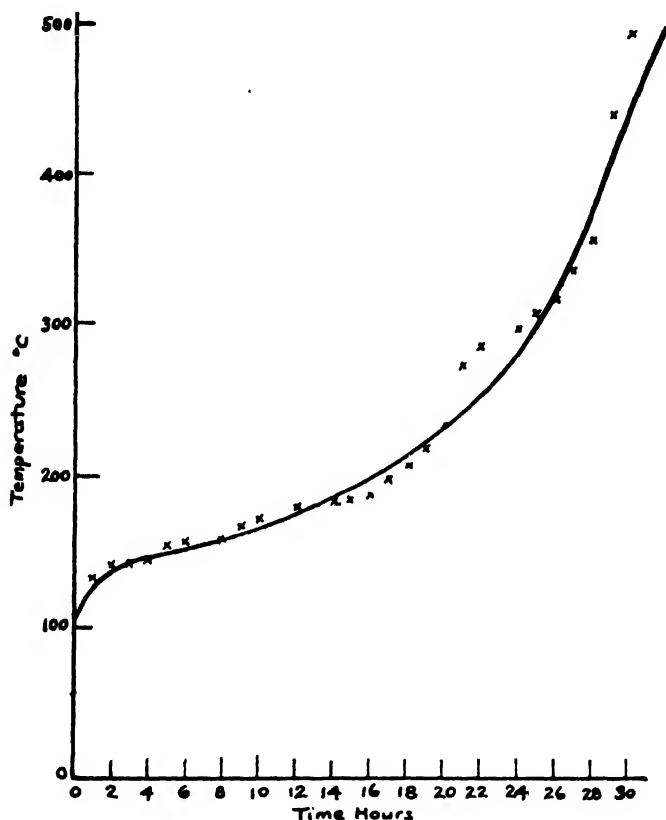
Fig. 78. Temperature of caustic in pot vs. time in hours.

Fig. 79 shows the time-temperature curve.

Again we note that except for a short duration at the start when dilute caustic is being boiled, the temperature of the caustic in the pot rises only slowly, but toward the end of the fusion operation when the specific heat of the more or less completely dehydrated caustic decreases, it rises rapidly.

Solid caustic is also made in a flake form or in a stick form, the former being frequently preferred by customers. It is made by scraping off the solid film from a rotating water-cooled cylinder immersed in molten caustic (Fig. 80), while the latter is made by casting it in molds. Powdered caustic is made by grinding the solid caustic. At present much of

TABLE 118. Temperature vs. Time Record During Fusion Operation.

Time (hrs.)	Temperature of Caustic (° C.)	Time (hrs.)	Temperature of Caustic (° C.)
1	...	38	257
2	72	39	260
3	74	40	265
4	83	41	270
5	93	42	270
6	116	43	280
7	145	44	280
8	148	45	285
9	155	46	292
10	159	47	300
11	162	48	310
12	167	49	315
13	168	50	325
14	170	51	330
15	173	52	340
16	175	53	346
17	177	54	352
18	180	55	363
19	180	56	377
20	182	57	398
21	185	58	420
22	188	59	440
23	191	60	457
24	195	61	463
25	199	62	466
26	200	63	461
27	201	64	451
28	205	65	445
29	207	66	430
30	210	67	420
31	215	68	405
32	218	69	396
33	220	70	387
34	232	71	375
35	250	72	370
36	251	73	360
37	255	74	342

the caustic is sold in liquid form containing about 50 per cent, or sometimes even 70 per cent NaOH.

This method of concentrating the caustic liquor to a molten state is rather wasteful of fuel. It is estimated that about 0.5 ton of coal is required under the pot to obtain one ton of solid caustic starting from the 50 per cent solution. Even when the strong liquor has been concentrated in the evaporators to 70 per cent NaOH, the fuel required in the pots still amounts to approximately 400 lbs. of coal per ton of solid caustic made.

Attempts have been made to do away with these fusion pots and substitute evaporators of a special design, or stills, using a liquid not miscible with NaOH. To obtain the required temperature for evaporation, the use for the heat vehicle of some working fluid other than steam, whose vapor has a high temperature at a comparatively low pressure, is very

essential, and diphenyl * offers some possibilities. Recently a process †
was developed for the concentration of 50 or 70 per cent liquid caustic by
a partial pressure evaporation in a steel evaporator, using kerosene of an
average boiling point of 431° F. The process may be carried out in a
nickel-clad still pot provided with an agitator and a closed-coil heater
using superheated steam or a high-boiling liquid. The ratio of kerosene
mixed with liquid caustic to caustic is 2:1, and the kerosene in the vapor
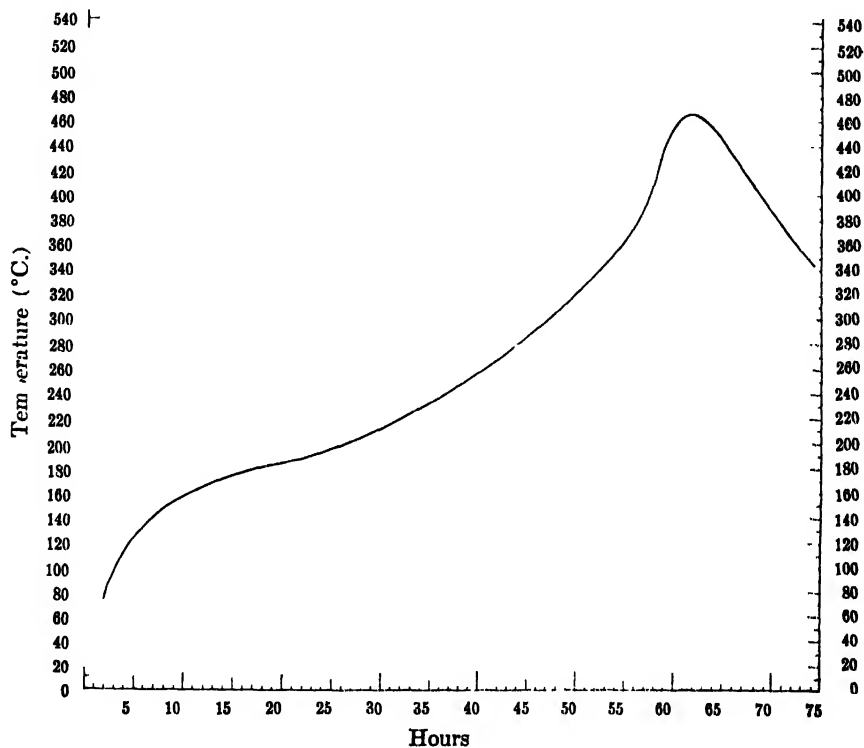
Fig. 79. Curve showing temperature of caustic in fusion pot.

phase is separated from the water in a condenser. A bubble-cap or
packed column may be provided on top of the pot still as a rectifier. The
weight ratio of kerosene and water in the vapor coming over into the
condenser is maintained at 7 parts of kerosene to 10 parts of water.
Crystals of caustic separate out in a very fine form of the size of 70-100
mesh in the kerosene slurry drawn from the bottom of the still and may

* Badger, W. L., Monrad, C. C., and Diamond, H. W., "Evaporation of Caustic
Soda to High Concentrations by Means of Diphenyl Vapors," *Ind. Eng. Chem.*,
July, 1930.
† "Anhydrous Sodium Hydroxide" by D. F. Othmer and J. J. Jacobs, *Ind. Eng.
Chem.*, Feb., 1940, pp. 154-160.

be separated from the kerosene by a centrifuge. Using a long cycle of 22 minutes in the centrifuge, it is possible to reduce the kerosene content in the caustic crystals to 1.8 per cent by weight or less. Caustic crystals from the centrifuge can further be washed with solvent naphtha until the residual kerosene content in the caustic is reduced to 0.1 per cent or less. The washed crystals are then dried at about 170° F. The naphtha-kerosene mixture is then separated in a fractionating column. Anhydrous caustic obtained in this way is fine, crystalline, and free-flowing, but may contain small amounts of kerosene and become discolored. The average
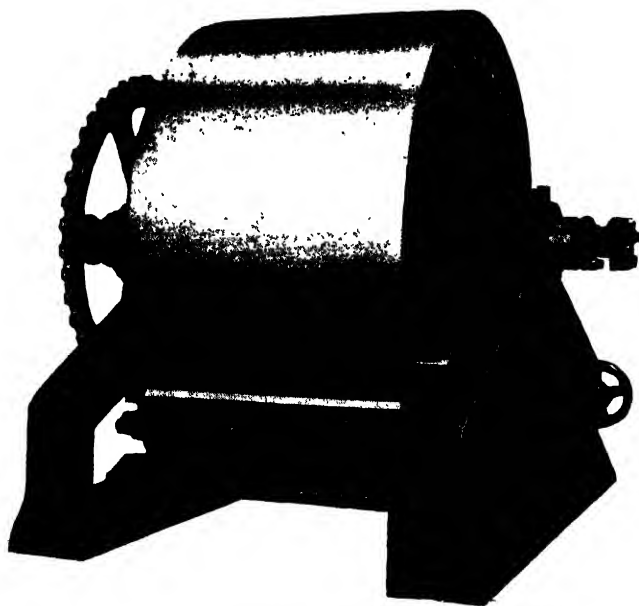
Courtesy Buffalo Foundry and Machine Co.

Fɪɢ. 80.   Caustic flaking drum.

temperature in the pot still is 423° F., and the heat required for dehydration is only about one-third of that required in ordinary caustic pot fusion. Compared with solid caustic in a large mass obtained by pot fusion, and packed in steel drums, these finely divided crystals have many advantages in industrial applications. However, a complete elimination of the last trace of kerosene from the caustic obtained is rather difficult and there may be objection in its use in certain industries where traces of kerosene are not tolerated. Also, the product may be colored gray unless a specially refined kerosene is employed and then used over again in the cycle. While the pot fusion process requires a temperature around 900° F. and is wasteful of heat and severe on the pots, the distillation method requires a temperature of only 430° F. and the heat efficiency is much better. Further, the operation by this partial pressure method may be made strictly continuous and carried out under a partial vacuum.

As has been mentioned before, caustic soda used for rayon manufacture must be of the highest grade and free from many impurities. For this, liquid caustic is generally supplied. Rayon and Cellophane manufacture by the viscose process require the digestion of some form of natural cellulose with caustic soda. The very rapid growth of the rayon industry has appreciably increased the market for caustic soda. Presumably, all impurities have a harmful effect in the viscose process, but any discussion of the production problems of rayon is beyond the scope of this book. There is an inherent and almost insurmountable difficulty in preparing the anhydrous material with negligible impurity content. Solutions up to 50 per cent NaOH by weight are much less corrosive, and a 45-50 per cent caustic solution has also a lower freezing temperature in this range as seen from the freezing point curve of the caustic soda solution (see Appendix). Consequently a 50 per cent solution is made and delivered to the rayon plant in a high degree of purity. For this reason and with the incentive of favorable freight rates established for tank-car lots, the growth of the rayon industry has brought with it a rapid increase in the quantity of caustic soda shipped by tank-cars as a 50 per cent solution. It also contributed to the commercial standardization of the 50 per cent strength.

The following analysis represents an acceptable liquid caustic.

TABLE 119. Chemical Analysis of Rayon Caustic ("50%" Solution).

Na_2O	37.4%
NaOH	47.3
Na_2CO_3	0.18
Al_2O_3 $\}$ Fe_2O_3 $\}$	0.02
NaCl	0.30
Na_2SO_4	0.15
SiO_2	0.34
CaO	0.01

In 1924 the rayon market took only a small fraction of the output from the chemical caustic plants, but in 1929 the rayon trade represented an appreciable portion. The effects of impurities were not yet understood but were commencing to be appreciated. By 1934 the demand for higher purity had increased in intensity. Quite remarkable decreases in the content of alumina, iron, and silica had already been achieved. The effort to reduce further the impurities of calcium, magnesium, sulfates, and heavy metals is still proceeding. Iron and silica have been the cause of the most frequent complaints. Lately, sulfates and alkaline earths, as affecting the clarity of the solution at low temperatures, have been receiving attention. Occasional complaints regarding impurities not even included in the analysis above have been made.

New laboratory technique and analytical methods have been introduced and are still being perfected in connection with this requirement of a high degree of purity. Even the spectrograph and accompanying light densitometer are now equipment for routine laboratory procedures.

Alkali manufacturers use two general schemes to produce such a high-grade liquor. The first is to use the purest of raw material and avoid all possible contamination of impurities (such as by the use of all-nickel evaporators, nickel-clad vessels, etc.). The second is to use various treatments or purifying processes on the finished caustic just before shipment. The method of manufacture gives rise to the presence of certain characteristic impurities in the liquid caustic obtained. For example, the electrolytic process, when using the diaphragm cell, introduces a unique problem with the NaCl. The mercury cell avoids this. The chemical (lime) process from ammonia soda ash introduces unique problems with sulfates. The heavy metals as impurities are common to all processes because of contamination from the concentrating apparatus. Competition on purity is extremely keen in America. The alkali manufacturers jealously guard their methods of producing pure caustic.
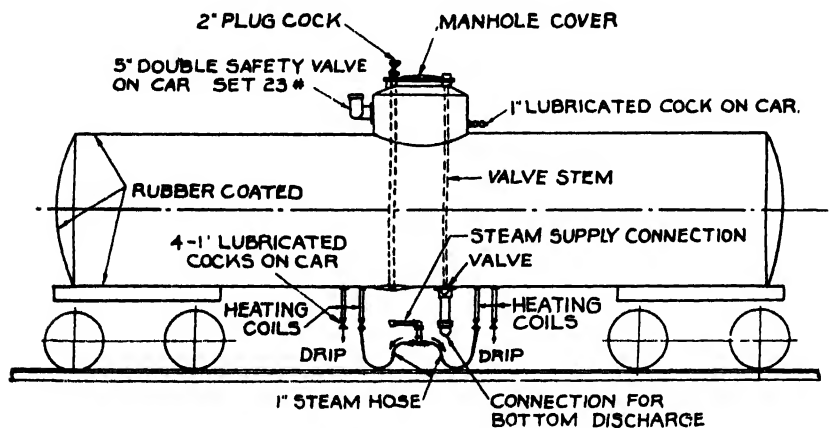
Fig. 81. Tank car for liquid caustic.

This very pure product cannot be shipped in ordinary iron tank-cars without acquiring very appreciable iron contamination during transit. A number of coatings which are principally rubber-base paint have been in use for several years for lining the insides of caustic tank-cars. A typical construction and arrangement of a caustic tank-car is shown in Fig. 81. It is equipped with steam coils for thawing the frozen content for unloading at sub-zero winter temperatures.

For the shipment of liquid caustic by water, a tank boat similar to an oil tanker has been used.

. Since attention was turned to the manufacture and use of liquid caustic in the industries, much investigation has been conducted to determine the thermochemical properties of caustic soda solutions, such as heat content (enthalpy) and specific heat (heat capacity) in relation to the concentration, temperature, and vapor pressure of caustic soda solutions. Merkel in Germany first studied these properties and in 1928-1929

published diagrams and tables. Later McCabe and Bertetti, at the University of Michigan, extended this study for concentrations from zero to 50 per cent NaOH and below 200° F.; and McCabe and Wilson further extended it to concentrations between 52 and 78 per cent NaOH in 1934-1936. These results may now be shown in Fig. 82.
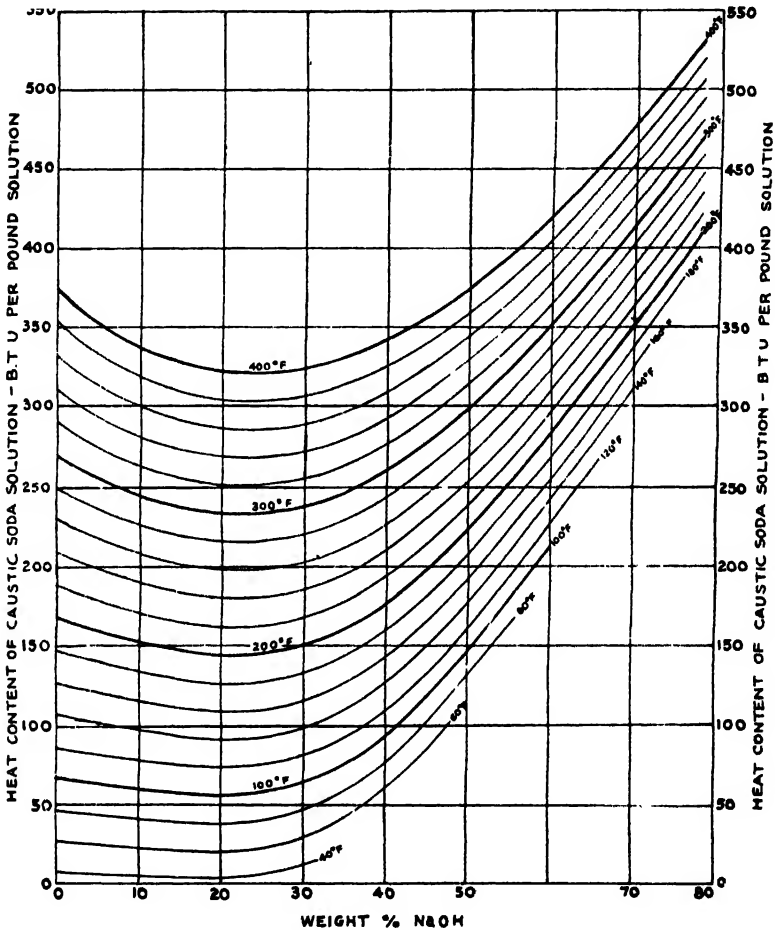
FIG. 82. Heats of dilution for caustic soda solutions (enthalpy chart).

Although certain data beyond the range of 50 per cent NaOH and above 200° F. are not yet final, these workers have given us a set of valuable data in a tabular form as a chart, that serves much the same purposes for the caustic soda manufacturers and users as the steam tables do for power plant engineers. This so-called Enthalpy-Concentration Chart (Fig. 82) has been a great help to all calculations in problems dealing with caustic soda concentration, evaporation, mixing and

dilution, and in the thermal effects of a caustic soda solution used as a medium in thermocompressor work. Details of physicochemical research, its method of attack, and its theoretical derivation cannot be entered into here, but the readers are referred to these original articles.* A Boiling
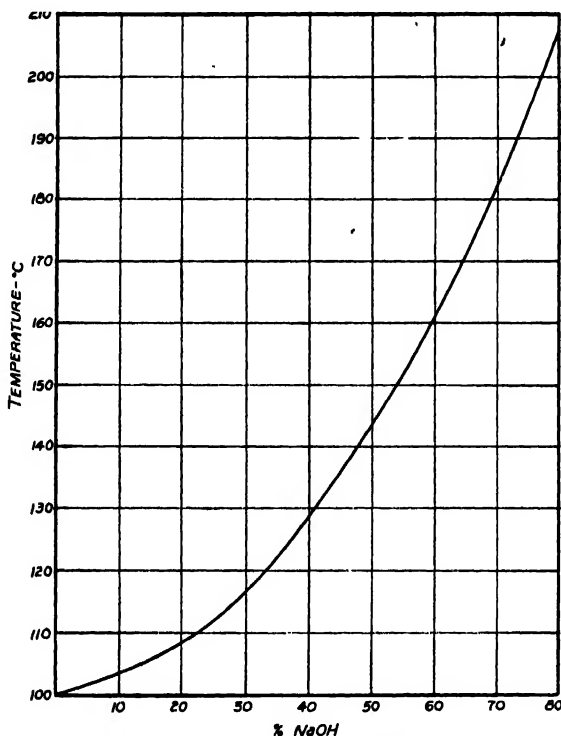
FIG. 83. Boiling point of caustic soda solutions.

Point-Concentration curve for solutions of sodium hydroxide at atmospheric pressure is given in Fig. 83. A specific heat table for caustic soda solutions of various concentrations is found in the Appendix.

It must not be supposed that since the advent of the electrolytic process

* Merkel, *Z. Ver. deut. Ing.,* **72,** 109 (1928).
Merkel, *Z. ges. Kälte-Ind.,* **35,** 130 (1928).
Merkel, *Arch. Warmewirt.,* **10,** 13 (1929).
Merkel and Bosnjakovic, "Diagramme und Tabellen zur Berechnung der Absorptions-Kältemaschinen," Julius Springer, Berlin (1929).
McCabe, W. L., "The Enthalpy-Concentration Chart—A Useful Device for Chemical Engineering Calculations," *Trans. Am. Inst. Chem. Engrs.,* **31,** 129 (Mar. 1939 for Nov. 1934).
Haltenberger, W., Jr., "Enthalpy-Concentration Charts from Vapor Pressure Data," *Ind. Eng. Chem.,* **31,** 783 (1939).
Bertetti, J. W., and McCabe, W, L., "Sodium Hydroxide Solutions," *Ind. Eng. Chem.,* **28,** 247-8 (1936).
Bertetti, J. W., and McCabe, W. L., "Specific Heat of Sodium Hydroxide Solutions," *Ind. Eng. Chem.,* **28,** 375-8 (1936).

TABLE 120. Production of Caustic Soda in the United States.*

Year	Chemical Process (short tons)	Electrolytic Process (short tons)	Total (short tons)
1921	163,044	75,547	238,591
1923	314,195	122,424	436,619
1925	355,783	141,478	497,261
1927	387,235	186,182	573,417
1929	524,985	236,807	761,792
1931	455,832	203.057	658,889
1933	439,363	247,620	686,983
1935	436,980 ·	322,401	759,381
1937	488,807	479,919	968,726
1939	530,907	494,104	1,025,011
1940 (Estimated)	500,000	595,000	1,095,000

' *Chem. Met. Eng.*, **48, 92** (1941); U. S. Census of Manufactures.

the quantity of the caustic soda made by the chemical (lime) process has been diminished. On the other hand, as Table 120 shows, chemical caustic production in the United States has been holding its ground, although the electrolytic caustic production has of late increased very sharply because of the demand for chlorine.

Fig. 84 shows the caustic production by the lime and electrolytic processes during the last two decades. From this it is clearly seen that the electrolytic production has now overtaken the chemical (lime) production.

Also, because of increased competition from the electrolytic caustic, the ammonia soda manufacturers themselves today have gone into the manufacture of electrolytic caustic. Since the advent of the alkaline-chlorine industry in the beginning of the present century, electrolytic
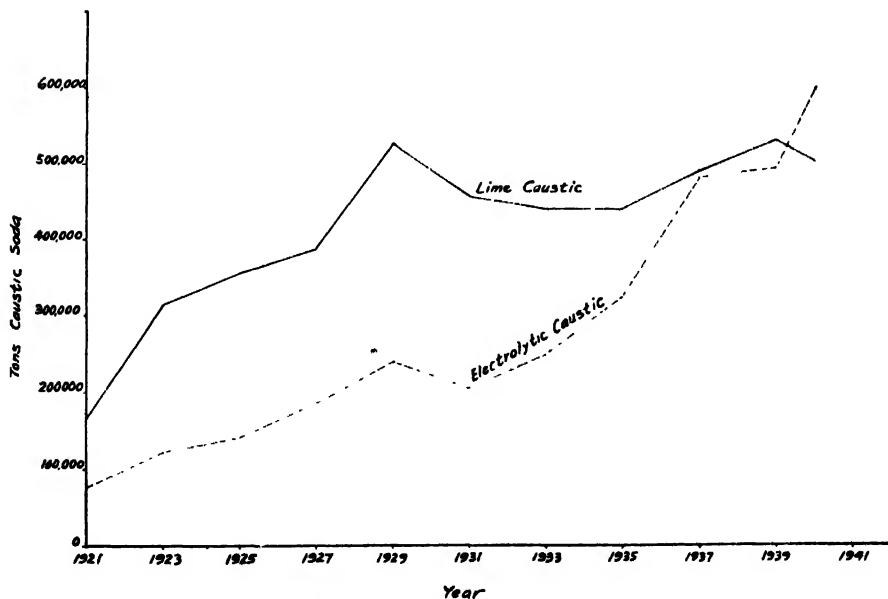
FIG. 84. Curves showing production of lime and electrolytic caustic.

caustic production in this country has come to the fore very rapidly, growing from a very insignificant production in 1910 to a point where its volume of production is now greater than that of chemical caustic. For this reason a chapter will be devoted exclusively to the electrolytic production of caustic soda and chlorine. (See Chapter XX.)

RECOVERY OF LIME FROM CAUSTIC MUD

In Fig. 76 we have shown a rotary kiln as a part of the equipment in the chemical caustic plant for reburning the caustic sludge. We shall now devote some space to the description of details concerning the recovery of lime from caustic mud.

The calcium carbonate precipitate resulting from the causticizing reaction between milk of lime and sodium carbonate solution is handled in one of three different ways:

(1) "Reburned" in long rotary kilns to recover lime for additional reaction.

(2) Sent to a by-product plant as raw material of cement manufacture.

(3) Sent to waste.

Of the total chemical caustic produced, probably at present more is made in plants employing the third method of disposal of the mud than either of the other two. This is explained by the fact that soda manufacture is most generally conducted where lime is very cheap. The tendency, however, is in the direction of installing more equipment for reburning. Cement is made only where there is a rather rarely occurring fortuitous combination of cement market, alkali industry, and the presence of other suitable raw materials for cement manufacture.

Regardless of the method by which the NaOH content in the precipitated mud is minimized, subsequent preparation of the material for feed to a reburning kiln is to get its moisture content as low as is economical. The physical character of these muds is such that a high degree of dryness is generally uneconomical, though not impossible, to maintain continuously. The calcium carbonate in the mud is present in a variety of forms. There are also present (in small concentrations) a number of double or triple compounds of calcium, magnesium, aluminum, iron and silicon, present as oxides, hydroxides, carbonates, chlorides, sulfates or silicates. They are generally in the forms of calcium or magnesium-aluminum silicates, carbonates and sulfates. Variations in the composition undoubtedly account for the large variations in moisture-retaining properties of the sludge.

In spite of the fact that the water in the sludge must be converted to vapor at the expense of additional fuel over and above that required in the simple decomposition of the carbonate to the oxide, it is probable that a high degree of dryness would bring about materially lower fuel consumption only if expensive heat recuperation equipment has to be added to the installation. Therefore, as in the cement industry where the "wet process" is, in actual practice, substantially as economical as the "dry process," the alkali operator strives for a consistency of 35 to 40 per cent

moisture. He is generally much more concerned with a low alkali content in his preparation of the muds for reburning, to avoid excessive attack on the refractory lining.

The kilns for reburning are essentially similar to those used in wet-slurry cement practice. A steel cylinder, 6 feet or more in diameter by 150 feet or more long, is set on a slope of about $\frac{1}{2}$ inch per foot. It is lined with refractory materials throughout its length, part of which may be backed by insulating materials. It is mounted for slow, controllable-speed rotation. The lower end is fitted with a hood carrying an adequate fuel burner with primary and secondary air inlets. This end is also arranged so that the lime discharged is removed continuously and automatically either by drag chain conveyors, or via a lime cooler and conveyors to storage. (See Fig. 85 for one type of rotary kiln.)

The high end of the kiln is arranged to discharge the gaseous products and to receive the feed of lime sludge. The gases are not recovered for soda manufacture. The upper half or third of the kiln length is fitted with "chains" in the usual fashion of a wet-process cement kiln. Such chains are interlaced lengths of common chain, the links generally being about 2-2$\frac{1}{2}$ inches long and of $\frac{3}{8}$-inch rod diameter. One end of a length is fastened to a point in the shell from the top in a position of 60° to the left of the vertical line. The opposite end of that chain-length is then fastened to a point in the top of the shell about 12 to 16 feet away axially and at 60° to the right of the vertical line. In an 8-foot diameter kiln standing in the 60°-to-the-left and 60°-to-the-right position, each loop of chain is long enough so that the bottom of the catenary is about two feet above the bottom of the kiln. At one axial location, from 12 to 24 chain lengths originate and generally two sets of lengths are staggered. As the kiln rotates these lengths dip into the mud which is slowly flowing along the bottom of the kiln and they emerge thickly coated with the mud, thereby forming a much extended, exposed surface between the mud and gases. This promotes drying and preheating of the calcium carbonate mud and at the same time the cooling of the gaseous reaction and combustion products. As the chains rub over each other, embryo lumps of lime are formed.

Another type of the chain section is made by fastening sections of the chain in planes perpendicular to the axis of the kiln at equidistant points on a number of angle-iron guide spirals attached to the shell of the kiln. The sagging of the chains between points of support causes them to dip into the mud and lift it in contact with the hot gases as the cylinder rolls over.

The chain section extends as far down the kiln as the conditions of operation will permit. If the chain section is carried too far down toward the fire, the chains will be operating at too high a temperature. They would not only be heated to destruction at that point, but also are objectionable in creating dust loss if the material is too dry.

If the chains do not extend far enough toward the fire end, there is no good heat interchange between incoming wet mud and combustion prod-
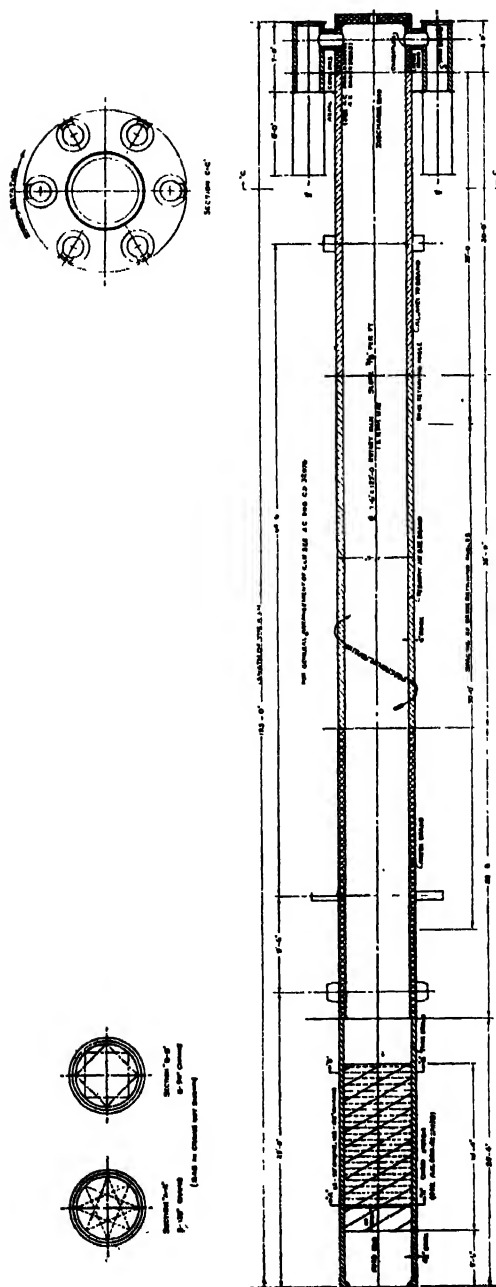
Fig. 85. Sludge recovery rotary lime kiln.

ucts, with consequent high fuel consumption. A more serious difficulty, brought about by insufficient number of chains, is the formation of "rings." At some intermediate state of dryness the physical characteristics of the mud in the kiln are such that the material agglomerates or clots into masses. These will at times adhere to the sides of the kiln where there are no chains to break them up and a ring of semi-baked material builds up and acts as a dam restricting the flow of slurry from above and introducing a high pressure drop from below.

Ring formation is not alone due to incorrect proportioning of the chain section. Variations in concentration of the impurities such as iron, alumina, silica, sulfate, etc., and particularly, alkali content also have a bearing on ring formation. Under good operating conditions the mass emerging from the chain section is more or less granular. It consists of lumps, varying from $\frac{1}{2}$ inch to $1\frac{1}{2}$ inches in diameter just perceptibly damp and with very little dust and no large lumps.

The best fire is in the nature of a long plumy flame. Pulverized coal or any powder fuel mixture with sufficient volatile matter to maintain a steady ignition state, is the most suitable. Natural gas, producer gas, or any kind of oil can be used if the proper burner design and burning conditions are provided. The choice of fuel depends almost entirely on local cost. Another factor occasionally affecting the choice of fuel has to do with the strength of CO_2 in the kiln gas. If Dry Ice or liquid CO_2 is being manufactured from these gases, the fuel which is richest in carbon has the advantage.

The gaseous products of calcination and combustion are cooled by the incoming wet mud, particularly in the chain section of the kiln. Depending on the cost of fuel, additional kiln length may be justified to cool these gases to low temperatures if an induced draft fan is provided. In usual practice they leave the high end of the kiln from about 230-350° F. At very low rates of operation in long kilns they may occasionally fall to the dew-point. The gas may contain from 18 to 30 per cent CO_2 on the dry basis, the strength depending mainly on the moisture content of the mud feed, the carbon content of the fuel, the excess air required, and the efficiency of the burner and kiln. It is a common practice to carry a slight excess of oxygen so that there will be substantially no CO.

The gases precipitate a portion of their dust burden in a chamber at the high end of the kiln and are then, by means of induced draft fans, exhausted through a suitable chimney. When a liquid or solid CO_2 operation is included, the gas is taken from the chamber just in front of the high end of the kiln.

Control of this operation is essentially similar to that of burning oyster shells in rotary kilns which is described in Chapter VI. Capacity, or rate of output, is controlled by kiln speed, and the fire is controlled by the combination of lime and gas analyses. The "wet kiln" operator has the additional problem of relatively large fluctuations in the content of moisture in the feed to his kiln, but on the other hand, he is less concerned with the quality of gas emerging from his apparatus.

The rate of operation of a reburning kiln must keep reasonably well in pace with the rate of operation in the caustic plant which it serves. The only latitude in out-of-step conditions is that which is provided for in storage reservoirs for:

(1) Washed caustic sludge
(2) Reburned dry lime
(3) Milk of lime at reburning plant
(4) Milk of lime at caustic plant

All these kinds of storage are relatively expensive. The dry lime storage requires elevators and conveyors for handling a seriously hot and abrasive material. Both the milk of lime and the unburned sludge storage require power-consuming agitation to maintain the material in suspension suitable for pumping.

Storage tanks must be adequate in size to take care of the usual operating difficulties. In case a breakdown in the recovery plant prevents continuation of the reburning, there might be a loss of sludge, were there no reservoir space to receive it from the caustic plant where it continues to settle out of solutions even for a long time after the reacting constituents are no longer fed. Likewise interruption of operation of the recovered lime slaking operation would require expensive slow-down or shut-down of the reburning kiln itself, if there were no place to store additional freshly burned lime. On the other hand, a break-down of moderate duration at the caustic plant should not require an immediate corresponding adjustment of the lime recovery operation.

The most frequent "operation" of the storages in such a system is to take care of variations in the settling rates of the causticizing precipitate. Probably for the same reasons as were advanced to explain the variations in moisture-retention characteristics, the rates of settling vary between wide limits. Only the most skillful operating engineers know the fine points of mud settling. Consequently, that portion of the mud which is at any one time held in the reaction vessels of the caustic plant also varies between wide limits. The handling of storages is one of the most difficult operations involved in the reburning operation. Expert design is needed to provide adequate storages which will not cause excessive power or maintenance costs.

The feed of slurry to the kiln is generally controlled with a "Ferris wheel" feeder similar to those used in wet-process cement practice. This consists of cups or buckets mounted on the rim of a wheel. The wheel is driven from the kiln by a synchronous tie which is connected to the kiln motor. The sludge is thus delivered to the kiln in an exactly controllable relationship to kiln speed.

Since there is a small and continuous loss of lime from the system, a lime "make-up" must be provided (see Fig. 76, p. 289). This can be lime from the kilns of the adjacent ammonia soda plant, or it can be fines of limestone from crushers to be fed into the kiln together with the caustic sludge. The kiln operator strives to maintain the loss at a minimum. Most of the losses occur at the kiln end of the system, substan-

tially none at the caustic end. The two essential sources of loss are in the dust carried off with the chimney gases, and in the undigested lumps rejected from the screen while the reburned material is slaked to milk of lime. The first loss is generally a function of rate of operation. At normal rates, it will be quite low, possibly $\frac{1}{2}$ to 2 per cent of the feed. When the apparatus must be forced to highest production, this loss assumes rapidly increasing magnitude.

The loss as slaker rejects has little to do with rate of operation. It is a function of impurity content and also of burning conditions. Certain kinds of silicates are formed in a material of this nature, particularly when the feed is insufficiently freed of alkali. Some of these silicates are very high in lime, but they digest in the slaker very slowly (if at all).

Occasionally a portion of the lime made from the reburning of the mud is purposely fed into the prelimers of the adjacent ammonia soda plant and fresh lime from the burning of quarried stone in vertical kilns from the ammonia soda plant is used as "make-up" in the caustic plant. By such an expedient, impurities such as sulfates, iron, alumina and silica can be purged from the system.

The burning of the lime is controlled to give the lowest cost of production for caustic. If there were nothing but fuel economy in the kiln to consider, a kiln could undoubtedly be designed to burn the material to a negligible percentage of residual CO_2 in the lime. This is very seldom done. It requires a higher temperature and protracted holding of the materials at the higher temperature. Under such conditions, the lime "shrinks" and becomes what is known as "dead burned." Such lime may have very poor reaction characteristics in the causticizing operation. It may react slowly and may produce a precipitate which settles very slowly and is difficult to wash free of alkali.

A "soft-burned" or fluffy lime generally contains from 4 to 8 per cent CO_2 or more. It frequently forms a "fat" milk of lime, that is, one having a very high relative viscosity. Such material is generally difficult to pump and frequently causes trouble in pipe lines when a high strength of milk of lime is desired.

Minimum CO_2 in the lime requires high investment in the kiln. Incompletely reburned mud does not generally involve large cores such as in vertical shaft kiln operation. Nor does it necessarily involve a high fuel loss, because the moisture evaporated per ton of caustic made is not strictly proportional to the moisture per ton of CaO burnt. A "quick-settling" lime of good filtering and washing properties may have contained 10 per cent CO_2 leaving the kiln, and may return to the kiln with lower moisture content than would a slimy mud obtained from lime burned to say 3 per cent CO_2.

A skilful lime recovery operator learns by long experience the peculiarities of the materials which he is handling. The successful and economical operation of the caustic plant depends on his skill, care, and vigilance.

Chapter XX

Manufacture of Electrolytic Caustic, Chlorine and Chlorine Products

As early as 1800 the electrolytic method of caustic soda manufacture was known, but it was not until about 1885 that successful commercial application was accomplished. Undoubtedly, the perfection of the direct current generator, or dynamo, contributed much to the success of the process. Now for more than four decades it has been an important method for the manufacture of caustic soda, chlorine, and chlorine products. Caustic soda produced by this process has become a product of standard purity in the chemical trade. Wherever electric current can be economically generated, either because of the cheapness of coal or rather because of the presence of abundant water power, the electrolytic method has found wide application. This is notably true of Niagara Falls. Cells of the diaphragm type are most commonly used for this purpose in the United States; the commonest ones are the Vorce, Allen-Moore, and Hooker S cells, although the mercury cells of the Castner type are fast coming into use in one modified form or another.

In Germany the horizontal Billiter-Siemens type cell is used very extensively. This type of cell has a horizontal diaphragm at the bottom, the caustic liquor produced at the cathode flowing away from the diaphragm under static pressure so that there is no chance for the caustic to come into contact with the anode above. This separation is aided by the increase in the sp. gr. of the liquor during electrolysis. Unlike the vertical diaphragm cells, the static head over the whole area of the diaphragm here is uniform. The diaphragm is made of sheet asbestos covered with precipitated barium sulfate and fine asbestos fiber. The anode disc is made of graphite, and the cathode consists of a lattice of iron or nickel wires. The cell liquor is maintained at 70 or 80° C. by means of stoneware heating coils.

Electrolytic cells using brine can be divided into three main classes:

(a) The diaphragm type, in which the cathode liquor is separated from the anode by means of an asbestos diaphragm. This class has many representatives and is by far the most commonly used in the United States. Some of these cells have already been mentioned above.

(b) The bell type, which has no diaphragm; but the brine is fed into the bell and flows out by gravity, thus keeping the cathode liquor from coming into contact with the anode. This class of cell is not in general use in the United States.

(c) The mercury cell, in which mercury is used as the cathode and an amalgam is formed with the metallic sodium. The amalgam is decom-

posed in the central compartment or outside chamber by water, forming almost pure sodium hydroxide solution in a rather concentrated form (sp. gr. about 1.3). A well-known representative of this type is the Castner-Kellner cell installed at Niagara Falls. One of the ammonia soda manufacturers (at Wyandotte, Michigan) also uses this type of cell. The Krebs cell is an outgrowth of this type.

It is not within the province of this work to describe each type of individual cell in detail. Suffice it to discuss a few of the typical cells which are most generally installed in this country, and their operation in detail.

In what follows, we shall describe in considerable detail the application of the process by means of the Allen-Moore cells of the vertical-diaphragm, rectangular type, which are widely used in paper and pulp mills throughout the United States; the Vorce cylindrical cells, which are now perhaps more extensively used than any other diaphragm type cells in the United States; and the Hooker S cells, which have been developed in large units with high electrical efficiencies and large output.

Brine. The brine used is a saturated salt solution made from rock salt. To prepare the brine, rock salt is charged to the top of a saturator, a tall square concrete tank about 6 feet square (inside dimensions) by 20 to 25 feet high, or in cypress tanks having a diameter of 30 to 40 feet and a height of 15 to 20 feet. The tank is kept full of salt. Water is introduced from the bottom of the tank; and as it forces its way to the top, it becomes saturated and flows from the outlet at the top as saturated brine. The amount of water passed in is so regulated that the overflow is saturated. Salt is constantly added to keep the tank full, and the mud that accumulates in the saturator is flushed out at intervals through the outlet opening at the bottom. Salt suitable for this purpose must be rather free from calcium and magnesium compounds and sulfates, and the brine made must be purified by chemical treatment before use; otherwise the diaphragms are likely to be clogged by the precipitated calcium and magnesium hydroxides in the cathode chamber. Of the two main impurities in the brine (calcium and magnesium), magnesium is the more objec-

TABLE 121. Analysis of Rock Salt.

	Per Cent
NaCl	98.50
Insoluble matter	0.57
Moisture	0.07
CaO	0.28
MgO	trace
SO$_3$	0.12
Fe$_2$O$_3$	trace

tionable, because magnesium hydroxide, unlike calcium hydroxide, cannot be washed out of the asbestos diaphragms by flushing with warm water. Renewals for the diaphragms must therefore be more frequent. This would shorten the life of the cells. It is clear that for this purpose rock

salt is superior to sea-salt obtained from solar evaporation, for the sea-salt usually contains more magnesium salts. Good rock salt should have the analysis given in Table 121.

The brine overflowing from the saturator should contain about 315 grams of sodium chloride per liter at a specific gravity of 1.20 at 25° C. Good, soft water (warm if it is available) is best for brine saturation in the saturator.

If rock salt brine is available from brine wells by pumping down water to dissolve the rock salt to saturation (or nearly so), the rate of pumping must be so regulated that such a concentration of brine shall be maintained. Natural brine in this country is frequently not saturated, and must be brought to saturation at the plant. Where such unsaturated brine is impure, it is generally evaporated in multiple-effect evaporators to crystallize out the salt in order to eliminate the impurities, and then the salt crystals are dissolved to make saturated brine.

The brine from the saturator or from the wells flows to storage tanks from which it is pumped, or flows by gravity, to the purifying tanks. These are usually cypress tanks 25 to 35 feet in diameter and 15 to 20 feet high, to which soda solution (10 per cent strength) is added in quantities sufficient to precipitate the calcium and magnesium compounds as carbonates, the solution being agitated by compressed air. The wash water containing caustic soda and salt (see below) is used to make the soda solution. Saturated brine made from precipitated salt (which carries some caustic) from the salt catchers at the bottom of the evaporators is best admixed to the raw brine in sufficient quantities to precipitate magnesium compounds as $Mg(OH)_2$. Soda ash alone does not precipitate all the magnesium unless a large excess is employed, and then the precipitate formed does not settle well. To aid settling, the brine can be heated to 140° F. by steam coils. This treatment removes the calcium and magnesium, but not the sulfate ions. To test whether sufficient soda ash and caustic have been added, take about a 100-cc. sample of the brine, filter it into a 100-cc. graduate containing 10 cc. Na_3PO_4 (10 per cent solution). Stir, and observe any cloudy appearance by looking down vertically through the solution. After a sufficient quantity of soda solution has been added as determined by this test, the brine is filtered through a sand filter constructed of wood and having a false bottom which is covered with burlap, over which is placed a 4-inch layer of coarse cinders, then a 2-inch layer of fine cinders, and finally about a 6-inch layer of clean, coarse sand. Mud collects on top of the sand and the clear brine flows to the acid-proof storage tanks. To prevent clogging of the filter the sand should be back-washed at intervals. The schedule for cleaning is to be determined by the individual plants. To save labor, the treated brine may be run through filter presses, such as those made by the Sweetland or other companies.

To correct the alkalinity in the treated brine, commercial hydrochloric acid is added to the acid-proof tanks in slight excess (about 3½ pounds of the commercial acid to every 1000 gallons of brine), and the solution is

agitated by compressed air. This acid reaction is necessary to prevent any hypochlorite formation in the anode compartment. From these tanks the acidified brine flows to a constant-level head tank and then to the individual cells through the float-feed control system. This treated and acidified brine has the composition shown in Table 122.

TABLE 122. Analysis of Treated and Acidified Brine.

Sp. gr.	1.196 at 20° C.
NaCl	315 grams per liter
HCl	0.15 grams per liter
Na$_2$SO$_4$	2.00 grams per liter
CaO	0.67 gram per liter
MgO	nil
Fe$_2$O$_3$	nil

Allen-Moore Cells (KML type). The detail of construction of these cells is shown in the accompanying photograph (Fig. 86) and cross-section view (Fig. 87).

To illustrate one typical installation, the following arrangement may be described. A 340-KW dynamo driven by a steam engine, Diesel engine, or A.C. motor, having a terminal voltage of 230 v. feeds the direct current through 64 such cells connected in series and arranged in two rows along each side of the room. The bus-bars connecting the anodes or graphite
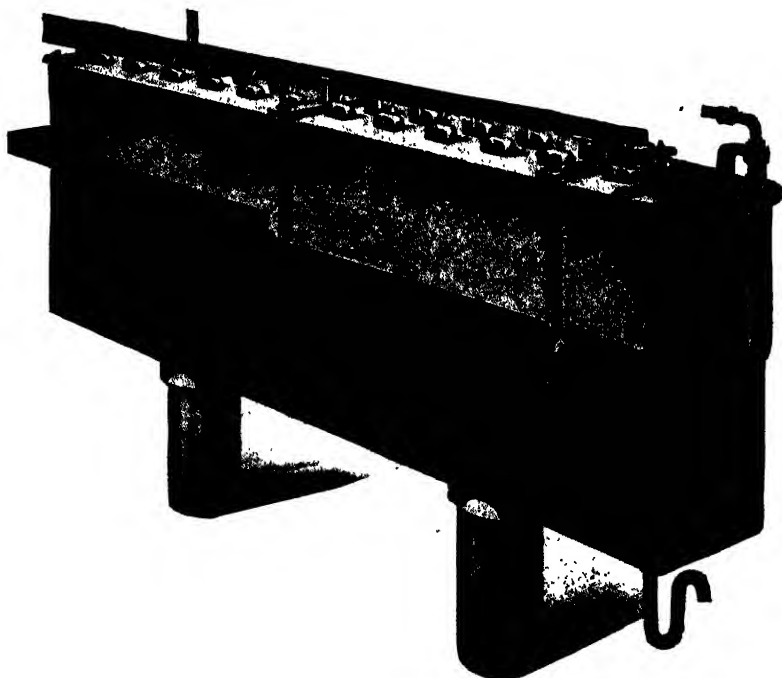
Courtesy Electron Chemical Co.

FIG. 86. The Allen-Moore cell.

electrodes are copper bars of varying cross-section, which are connected to each graphite electrode by means of a copper wire. There are 24 of such graphite anodes arranged in two rows with 12 on each side. These anodes are placed close to the perforated iron sheet cathode and are separated by asbestos sheets, which serve as the diaphragm supported by the cathode. The gap between the cathode and the anode surface is about ¼ inch, and the lower ends of the graphite anodes are separated from the
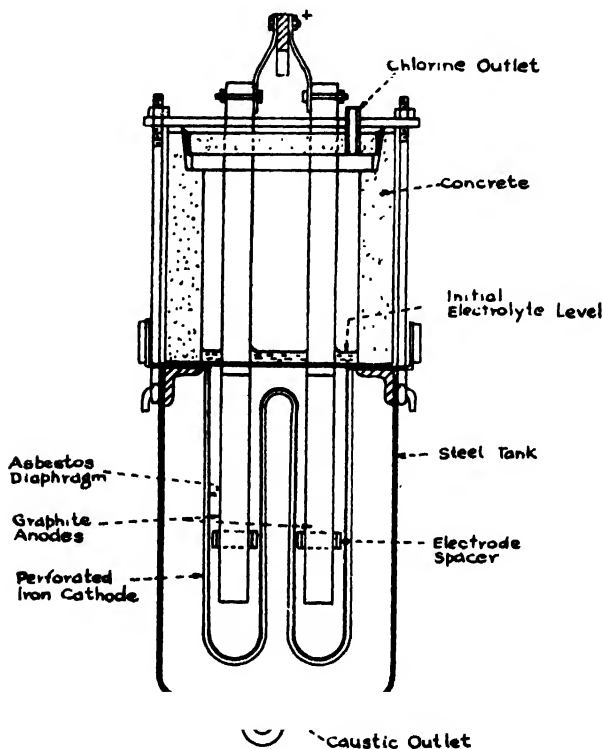
FIG. 87. Allen-Moore type KML alkali-chloric cell.

cathodes, and from each other, by means of porcelain spacers. From the anodes, the current travels through the brine, and through the asbestos diaphragm supported by the cathode, which in the KML type is W-shaped. From the cathode the current is collected by another bus-bar which delivers it to the graphite anodes of the cell next in series, and so on. Enclosing the perforated iron sheet and the graphite anodes is a space, or cathode chamber, in which the electrolyzed brine collects and drains out of the cell through a U-loop seal at the bottom. The cathode chamber is a steel tank enclosing the W-shaped perforated iron cathode, and carries near the top of the tank a vent type for the exit of the hydrogen gas. (See cross-section view, Fig. 87.)

The anode chamber, which is set on the top of the steel tank, is con-

structed of carefully deposited concrete, consisting of 1 part cement to 3 parts clean stone or quartz crushed to about $\frac{1}{4}$-inch size. The inside surface of the concrete is painted with a coal-tar protective paint. On the top of the concrete anode chamber is located the chlorine outlet. The anodes consist of individual Acheson graphite boards $1\frac{1}{4}''$ thick $\times$ 30'' long $\times$ 6''-8'' wide. Joints, if any, are to be carefully machined and fitted together to minimize voltage drops. These graphite anodes last from 12 to 18 months, and the asbestos diaphragms last from 12 to 18 weeks.

The cell effluent has the composition shown in Table 123.

TABLE 123. Composition of Cell Effluent.

Sp. gr.	1.21-1.22 at 25° C.
NaOH	100-110 grams per liter (8.5-9.0%)
NaCl	180-190 grams per liter (15.0-15.5%)
Na₂SO₄	10-12 grams per liter (0.8-1.0%)

The reactions involved are as follows:

$$NaCl \rightarrow Na^+ + Cl^-$$
$$2Na^+ + 2 \text{ faradays} + 2H_2O \rightarrow 2NaOH + H_2$$
$$2Cl^- + 2 \text{ faradays} \rightarrow Cl_2$$
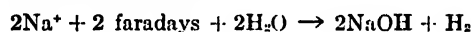
so that, apart from secondary reactions, hydrogen gas is evolved at the cathode where NaOH is formed, while chlorine gas is given off at the anode. The brine passes through the asbestos diaphragm, is electrolyzed at the iron cathode and flows off, carrying with it a large percentage of undecomposed salt so that NaOH may not furnish OH⁻ ions carrying the electric current to the anode.

$$NaOH \rightarrow Na^+ + OH^-$$
$$2Na^+ + 2 \text{ faradays} + 2H_2O \rightarrow 2NaOH + H_2$$
$$2OH^- + 2 \text{ faradays} \rightarrow H_2O + 1/2O_2$$
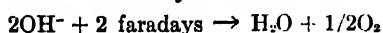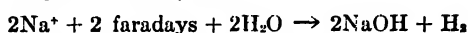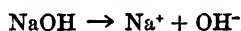
For if the last reaction is allowed to take place, it would cause loss of current as far as chlorine and caustic soda production is concerned, and so decrease the current efficiency. Besides, the oxygen thus formed would attack graphite, resulting in a short life for the graphite anodes and also in the contamination of the chlorine gas obtained. This is also true when much sulfate is present, as the SO_4^{--} ions would tend to carry current to the anodes liberating oxygen at the anodes. It is to prevent these excessive losses that electrolysis is stopped when less than one-half of the total sodium chloride in the brine has been converted to sodium hydroxide. As chlorine gas is fairly soluble in brine, if it for some reason comes into contact with sodium hydroxide, either hypochlorite or chlorate will be formed, according to the temperature conditions, as follows:

$$2NaOH + Cl_2 \rightarrow NaClO + NaCl + H_2O \text{ in the cold}$$

but
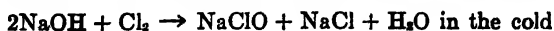
$$6NaOH + 3Cl_2 \rightarrow NaClO_3 + 5NaCl + 3H_2O \text{ in the hot.}$$
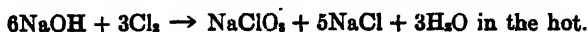
Either HClO or $HClO_3$ will attack graphite anodes, producing CO_2; therefore a small amount of sodium carbonate is always found with the caustic in the cell effluent.

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O$$
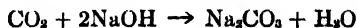
The theoretical voltage required can be roughly calculated from the following thermochemical equation, although the result is not strictly accurate thermodynamically.

$$2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + Cl_2 + Q; \quad Q = -H$$
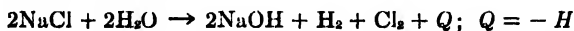
Heat of formation of 2NaCl in aqueous solution = $2 \times$ 96,600 cal.
Heat of formation of 2NaOH in aqueous solution = $2 \times$ 112,450 cal.
Heat of formation of $2H_2O$ in liquid state $\quad = 2 \times$ 69,000 cal.

$$\therefore Q = 2 \times - 53{,}150 \text{ cal.}$$

$$E = \frac{2 \times 53{,}150 \times 4.187}{2 \times 96{,}540} = 2.3 \text{ volts.}$$

Strictly speaking, we have to use the Gibbs-Helmholtz equation, expressing the relationship between the voltage and the heat of reaction, plus a temperature-coefficient term. The Gibbs-Helmholtz equation is

$$E = \frac{-H}{NF} + T \frac{dE}{dT}$$

where E = decomposition potential in volts.
   H = heat of reaction in joules for N gram equivalents of the substance = $4.185 \times$ No. of cal. per N equivalents. H is positive when heat is absorbed and negative when it is evolved.
   F = 96,540 coulombs per gram equivalent.
   T = absolute temperature in degrees Kelvin at which the current is passed through.

Separating variables we get

$$\frac{NF}{NFE + H} dE = \frac{dT}{T}.$$

Integrating between limits we obtain,

$$\frac{E_2}{T_2} - \frac{E_1}{T_1} = \frac{-H}{NF} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

This assumes that the heat of reaction H between T_1 and T_2 within not too wide a range of temperature is substantially constant. N and F being constants, if H is known and assumed constant, the decomposition voltage at any other temperature can be found from a known value at a given temperature. It will be seen that the above voltage of 2.3 ($=E$) is obtained by neglecting the temperature-coefficient term $T \dfrac{dE}{dT}$ and calling

$$E = \frac{-H}{NF} = 2.3$$

This is the minimum voltage. The actual voltage required is much higher, because of the cell resistance and of the polarization at the elec-

trodes. In practice, 3.5 volts is close to the average figure for this type of cell. Some energy is dissipated as heat by the resistance of the electrolyte. To minimize such losses, *i.e.*, to secure highest energy efficiency, the resistance through the electrolyte is reduced by placing the electrodes as near to each other as possible (about ½-in. clearance); by having the electrode surface as large as possible (about 25 sq. ft. to each cell); and by running the electrolyte rather hot (about 45° C.). It is understood that the electrolyte should be saturated to start with.

To cut out a cell, the current is short-circuited by clamping a copper bar onto the carbon anode bus-bar on the cell to be cut out and connecting it to the anode bus-bar of the next cell. The brine level in the cell is maintained constant by means of a glass float valve. Brine is fed from a cast-iron header from a head tank to the anode compartment, the header being provided with a tee for each cell, connected by a nipple next to the rubber valve which carries a flexible rubber tubing for delivering brine to each cell. The weak liquor, or cell effluent, from each cell is drained continuously into an open concrete trough and then to weak liquor storage tanks. Hydrogen gas is let out into the room through a vent pipe on top of the cathode chamber, or else it is collected and compressed for use. In some plants, hydrogen gas produced this way has been utilized for the hydrogenation of oils. Hydrogen is often burned with chlorine to make synthetic hydrogen chloride. With the development of the synthetic ammonia process by direct union between hydrogen and nitrogen gases, hydrogen gas from this source is now an important raw material. Chlorine gas is collected through a 6-inch stoneware pipe located above the anode compartment, and is drawn by means of a stoneware exhauster or a lead-coated steel fan through the absorption towers or bleaching powder chambers. The top of the anode chamber is covered with cement-asbestos bricks and the whole is luted over with a coal-tar cement or rubber-wax composition to prevent leaking of air into, or of chlorine gas out of, the anode chamber.

The voltage across each cell is taken once a day and the cell effluent tested for strength of caustic and the presence of hypochlorite. Current efficiency may be determined from the gas test with an Orsat. Systematic records are kept of each cell. The asbestos diaphragms gradually become clogged by solid deposits from the electrolyte, and the resistance to the flow is thus increased. To maintain the constant flow, therefore, it is necessary to raise the float and run a higher static head of electrolyte on the diaphragms. With new diaphragms in a cell newly cut in, the rate of flow may be as high as 35 liters per hour, but in the course of time it gradually diminishes to 20 liters per hour. Efficiency tests show that with a total current of 1500 amperes passing through the cells, the volume of effluent should be from 20 to 22 liters per hour. At the end of about 16 weeks, the asbestos diaphragms may become so badly choked that proper flow cannot be maintained with the brine level at the highest point. It is then necessary to cut the cell out, remove the asbestos, and clean the iron plates. A new diaphragm is made with three layers of asbestos

paper for the bottom half and two layers for the top half. After a cell has been cleaned and assembled with new diaphragms, the brine is fed in. When the electrolyte has reached the top of the cathode plate and normal flow has been reached, then and only then, should the cell be cut in. At first, when the cell is cold, the resistance is high, and the voltage drop across the cell is temporarily excessive. But as the cell is warmed up, this voltage will drop to 3.3 volts and then rise up gradually to about 3.45 volts. On the other hand, the new asbestos diaphragms being open, the flow for the first few days will be high, causing excessive amounts of unconverted salt in the cell effluent for a short time. As the diaphragm becomes clogged, however, the flow is diminished. After three or four months of continuous running it may fall below 16 liters per hour. This is about the time to change the asbestos diaphragms, as the reduced rate of flow would cause the formation of considerable hypochlorite or chlorate in the anodic liquor and reduce the current efficiency. Oftentimes, the addition of hydrochloric acid to the feed helps prevent the formation of hypochlorite.

It is often inadvisable to maintain a very high decomposition of brine in the cell effluent. For, in the first place, a high decomposition may be brought about by increasing the thickness of the asbestos diaphragm, thus decreasing the volume of flow of the effluent; in which case, the resistance to the passage of the current would be increased, with consequent loss of energy. In the second place, a high decomposition may be brought about by forcing a larger current through the cells; in which case, the cell terminal voltage would rise, causing a lower power efficiency and more vigorous oxidation of the graphite anodes by the oxygen liberated. Low percent decomposition of the brine, on the other hand, increases the cost of evaporation, especially if the fuel in the locality is expensive. Therefore, there is an optimum per cent decomposition based on the cost of the electric power vs. the cost of the fuel. With a high power cost and low fuel charges, the decomposition can be advantageously kept low; whereas with a low power cost and high evaporation charges, the decomposition should be kept high.

The current density employed in these cells is about 0.4 ampere per square inch. The current efficiency is 94 per cent, and the power efficiency is about 62 per cent. The decomposition efficiency of NaCl is less than 50 per cent. Some of the operating results of these cells are tabulated below:

TABLE 124. Some Typical Results of Allen-Moore Cells.

Sp. gr. of liquor	1.21
Percentage of NaOH in liquor	8.7
Percentage of NaCl in liquor	15.3
Caustic soda per cell per day	110 lb.
Chlorine per cell per day	98 lb.
Current per cell (approx.)	1500 amp.
Voltage per cell	3.5 v
Active anode surface per cell (approx.)	25 sq. ft.
Current density (approx.)	55 amp. per sq. ft.
Current efficiency	94%
Power efficiency	62%

In analyzing the losses of voltage in the cell, it may be stated that the theoretical decomposition voltage requires **2.3** volts, the over-voltage necessary (due to polarization, etc.) takes about **0.5** volt, and the ohmic resistance of the cell (**0.0005** ohm at **1500** amperes) makes an IR drop of **0.7** volt, giving a total of **3.5** volts for the terminal voltage across such a cell.
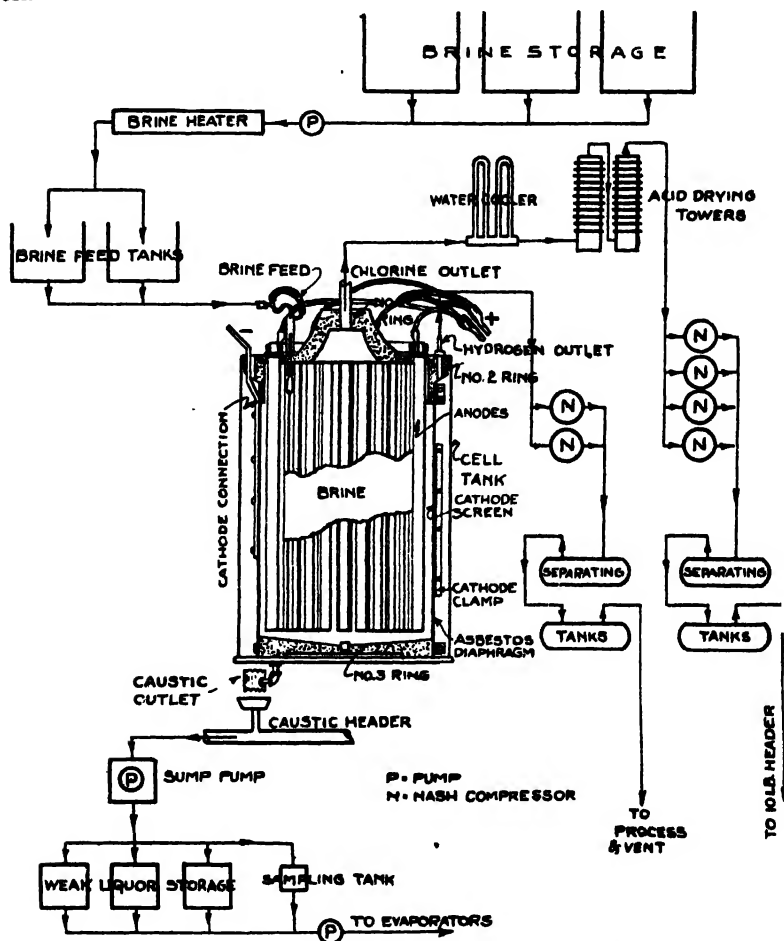
Courtesy Dr. L. D. Vorce

FIG. 88.   Cross-section of Vorce cell with flow-sheet diagram.

Recently the Vorce cells have been making great headway and are now in certain cases replacing the rectangular type of cell. The Vorce cell is of circular type (Figs. 88, 89 and 90), but it differs in no essential details either in principle or in materials of construction from the other vertical diaphragm 'cells. It consists of a circular steel tank (made of $\frac{3}{16}$-inch steel plate), a circular steel screen as the cathode, and a circular

row of 24 two-inch square graphite sticks 36 inches long as anodes, with a vertical asbestos diaphragm on the inside of the steel cathode screen. These anodes are suspended from the cover ring. The cover and bottom of the cell are made of cement, sand, and asbestos fiber, mixed in proper proportions with water and formed in wooden moulds. After these cement rings have taken an initial set, they are dipped in tar solution for water-proofing. The inside dimensions of each cell are 22 inches diameter by 34 inches high, and the overall outside dimensions are 26 inches diameter by 42 inches high. Its chief advantages over the rectangular type are: (1) the
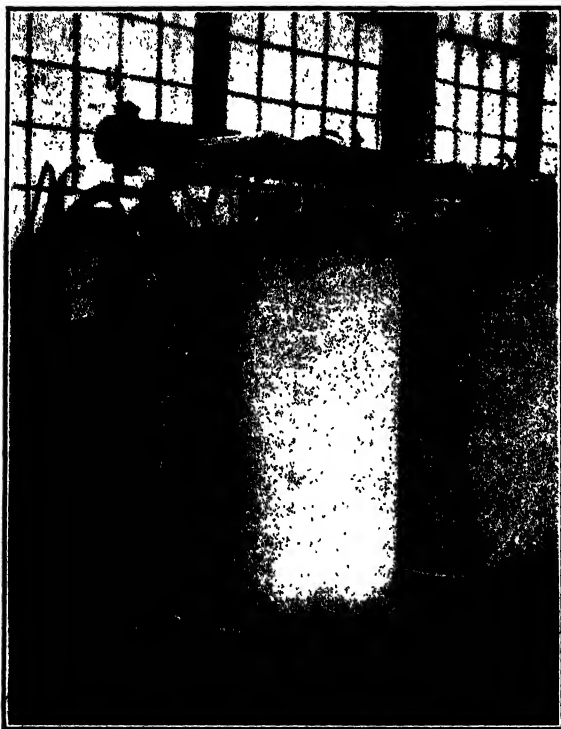
Fig. 89.

'End cells in series showing feeder connections to anode and cathode.

Courtesy Dr. L. D. Vorce

saving of the floor space (the saving being from a third to a half for the same capacity); (2) the larger anode surface and the integral construction of the anodes resulting in a smaller anode current density and lower resistance, and consequently in a high current efficiency, and low terminal voltage; (3) the simplicity and strength of construction resulting in the lightness of weight per unit of the cell output and in the saving of the massive concrete otherwise required; (4) the ease with which repairs and renewals may be effected by lifting off (if necessary) the whole cell bodily for working, each cell empty of the brine weighing only a little more than 500 lbs.; (5) the high purity of chlorine gas obtained (97-98 per cent), which is advantageous when liquid chlorine is to be made from the gas.

Consequently, Vorce cells are now probably more extensively used in the United States than any other diaphragm cells What was said above about the rectangular type of cell, however, applies equally to the Vorce
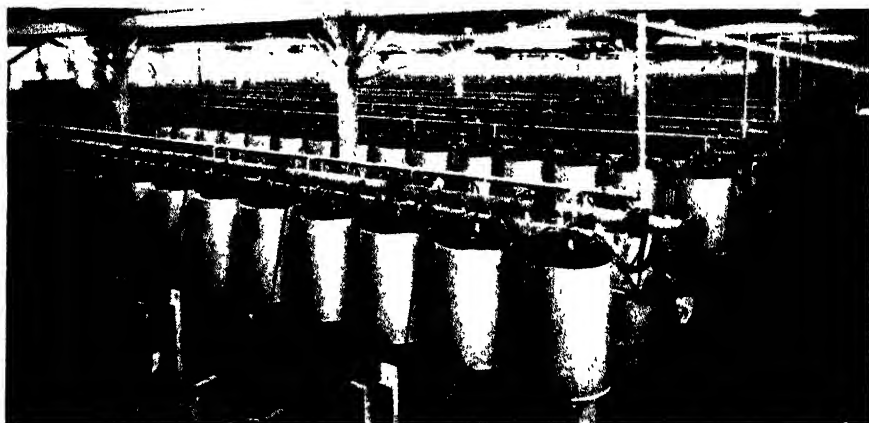
Courtesy Dr. L. D. Vorce

FIG. 90. Cell room containing many Vorce cells.

cells, so that no detailed description of their operation and maintenance will be given here, except that the anodes in the Vorce may last somewhat longer (18 to 20 months) and the life of their diaphragms is from three to four months between successive renewals. The life of the anodes may be increased considerably by treating the graphite with linseed oil. The conversion of sodium chloride in the Vorce cells is also the same as in the rectangular type of cell (105 to 115 grams sodium hydroxide per

TABLE 125. Average Results of Monthly Test Runs on Vorce Cells.

(Westvaco Chlorine Products, Inc.)

Sp. gr. of liquor	1.211
Percentage of NaOH	8.607
Percentage of NaCl	15.79
Percentage of Na_2CO_3	0.115
Percentage of NaClO	trace
Percentage of $NaClO_3$	0.068
Percentage of Cl_2 in gas	98.3
Percentage of CO_2	0.7
Gallons (U. S.) of liquor per cell per hour	3.417
Pounds of caustic per cell per day	71.42
Pounds of chlorine per cell per day	63.15
Pounds of caustic per kilowatt hour	0.859
Pounds of chlorine per kilowatt hour	0.793
Pounds of caustic per kilowatt day	21.42
Pounds of chlorine per kilowatt day	19.08
Average amperes per cell	948.1
Average volts per cell	3.5
Temperature of brine (° F.)	147.
Current efficiency (%)	94.84
Power efficiency (%)	62.11

liter). The Westvaco Chlorine Products, Inc., South Charleston, W. Va., which controls the sale of the Vorce cells, gives the data in Table 125 for the monthly average on the cells installed in their plant.
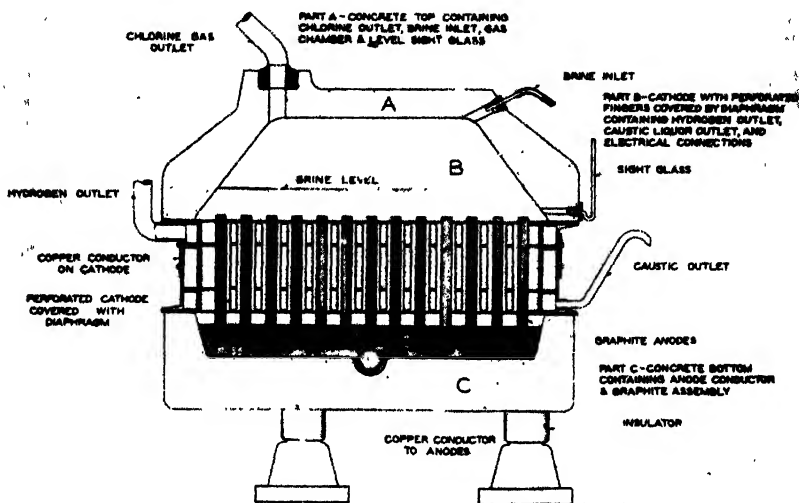
Courtesy Hooker Electrochemical Co.

FIG. 91. Hooker S type cell.

A new development in the construction of the Vorce cells consists in the addition of an extra cathode inside the row of anodes, which adds about 60 per cent more cathode surface and which also reduces the gap between the anode and cathode surfaces. This further reduces the terminal voltage per cell. It is possible that a working average voltage per cell of about 2.9 volts may be maintained with the same current capacity, thus increasing the power efficiency to 70 per cent. The capacity of the cell may also be increased up to 2500 amperes and the throughput doubled, without exceeding the present voltage of a standard cell. However, the current efficiency is lowered because of higher current density and a much higher current concentration (current concentration is defined as current throughput in amperes per liter of the volume of cell liquor).

From the old Townsend cell (Hooker Type F cell) have been developed the Hooker Type E cell (1913) and later (1929) the Hooker Type S cell [*] which has been installed in the Hooker Electrochemical Co. of Niagara Falls, N. Y., and works very successfully. It is almost a square type using concrete and steel construction (concrete bottom and top, steel middle section, see Figs. 91, 92, 93). The cell is insulated to maintain a

[*] Stuart, Lyster, and Murray, "The Story of the Hooker Cell," *Chem. Met. Eng.*, **45**, 358 (1938).
   Murray, R. L., "Growth of Electrolytic Alkali and Chlorine Industry in the U. S.—Development and Importance of Deposited Diaphragm Cell," *Trans. Am. Inst. Chem. Engrs.*, **36**, 445 (1940).

high temperature in the cell brine and is provided with a double-walled coil for heat exchange between the effluent and the incoming brine feed. Hence the electrical resistance through the electrolyte is low and a higher concentration of caustic is possible in the electrolyzed brine—as much as 135 g. per l. The distinctive features of this cell are the deposited asbestos diaphragms and the compactly arranged alternate anodes and cathodes filling the space inside the cell, so that the total anode or cathode area is more closely proportional to the cube, rather than the square, of the linear dimension of the cell. Further, the anodes are not supported from the top and there is no anode or cathode portion exposed to the gas space above

Fig. 92. Hooker S type cell with anodes in place ready for cathodes.

the liquor. The anode graphite blades are embedded in a lead slab at the bottom of the cell, while the cathode iron "fingers" are supported horizontally from the steel side frame. There are 28 of the cathodes and 30 of the anodes, arranged symmetrically on each side of the cell, leaving a central lane at right angles to the plane of electrodes for the brine

passage. The anodes are thus submerged in the cell brine, leaving the top cover entirely free, so that it may be conveniently lifted off. Thus the assembly of the cell can be inspected and spacing between each adjacent anode and cathode checked, before the cover is put on. The cell outside dimensions are 4 ft. 6 in. wide, 5 ft. long, and 3 ft. 8 in. high; they occupy a floor space of about 70 sq. ft. each, including all surround-
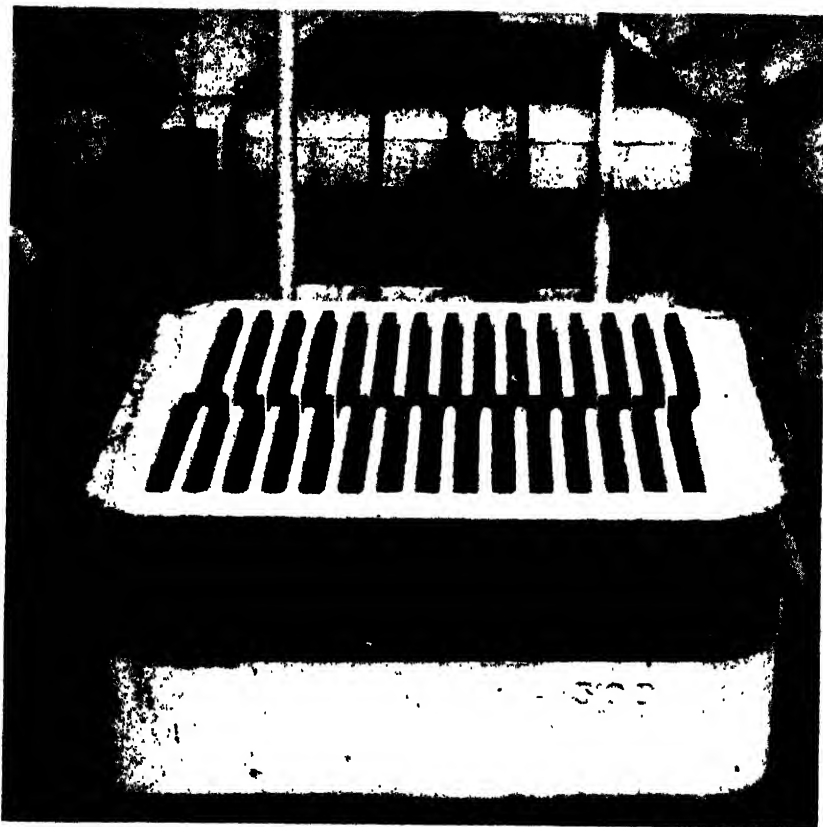
Courtesy Hooker Electrochemical Co.

Fig. 93. Hooker S type cell, anodes and cathodes in place.

ing working spaces. Each cell is able to take 6000-7000 amp. as working average and has a large output and high electrical efficiencies. These Hooker S type cells are coming into more and more extensive uses so that more chlorine will soon be produced by this type of cell than by any other in the country. Variable terminal voltage is used depending upon the age of the cell. Table 126 gives the average operating results.

We shall briefly describe the mercury cell which is not a diaphragm type but which is coming into use more and more extensively. The Michigan Alkali Company, Wyandotte, Mich., and the Mathieson Alkali

TABLE 126. Typical Operating Results of Hooker S Cells.

Current per cell	6000-7000 amp.
Voltage per cell	3.35 v.
Temperature of cell liquor (preheated brine)	90° C.
Current efficiency	95%
Voltage efficiency	69%
Power efficiency	65%
Active cathode surface per cell	130 sq. ft.
Active anode surface per cell	110 sq. ft.
Caustic soda in effluent	135 g NaOH per
Lb. NaOH per cell per day	452-530
Lb. Chlorine per cell per day	400-470
Life of anodes	450 days
Life of diaphragm	200 days
Chlorate formation per 1000 lb. NaOH	2 lb.

Works, Inc., Niagara Falls, N. Y., both have this type of cell in some modified form. In the original Castner cell, the body was made of slate or concrete, having the general dimensions: 4 ft. by 4 ft.-6 in. high. The anodes were the graphite blocks placed at the end compartments, while in the central compartment iron grids were used as the cathode. At the bottom of the cell, mercury was used as a sort of "intermediate electrode." In the end compartments, brine was electrolyzed and chlorine was liberated at the anode, and sodium was amalmagated with mercury at the bottom. At intervals, the cell was rocked by a cam mechanism and the amalgam from each end compartment was caused to flow to the central compartment where sodium in the amalgam came into contact with water, forming sodium hydroxide and liberating hydrogen gas at the iron grid cathode.

$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$
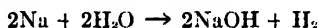
The only criticism about this cell was the rather small capacity per cell at that time and the expensive material (mercury) used. At present sev-

Year.
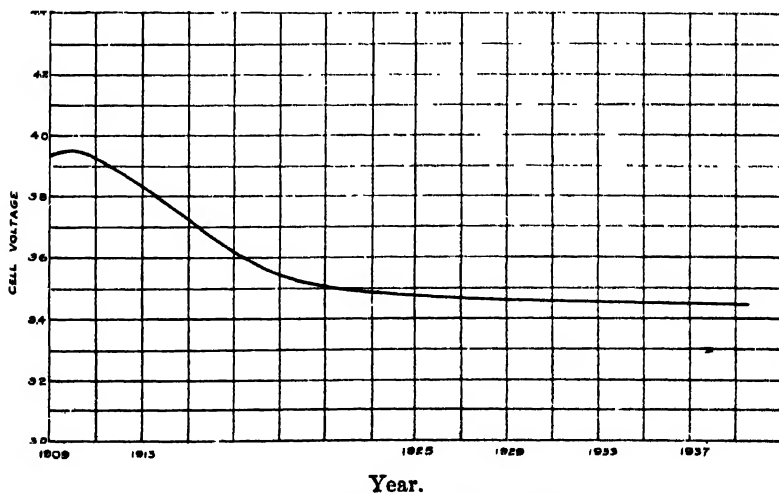
FIG. 94. Curve showing terminal voltage per cell.

eral modifications have been developed, some of them having a very large output per unit. One of them is the Sorensen cell which is not much different from the original Castner cell. It is constructed of a cast-iron frame lined with concrete. The liquor contains 20 per cent NaOH and the caustic made is very pure. The terminal voltage for each cell is 3.9-4.3 volts, averaging 4 volts. Another modification is the Krebs type cell which uses ebonite and iron frame for its construction. It takes a very large current—as much as 15,000 amp. per cell—and has thus a tremendous output. In these later modifications, mercury is used directly as the cathode and the amalgam is taken to a denuding chamber for decomposition. The advantages of these cells are that the caustic made is practically free from salt (NaCl) and has a higher concentration, thus reducing the cost of evaporation. A pure product is thus obtainable for rayon manufacture.
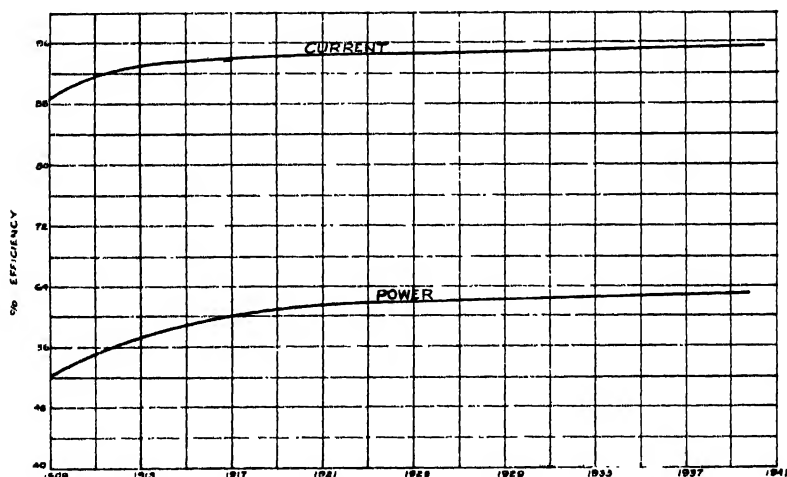
Fig. 95.   Curves showing power and current efficiencies.

Considerable advance has been made in the design and operation of the alkaline chlorine cells of the vertical diaphragm type, resulting in the reduction of the terminal voltage and in the increase of the power as well as current efficiencies. Indeed, electrical power and salt are the two largest items of cost entering into this electrolytic production of caustic and chlorine, amounting to fully two-thirds of the total cost of production, so that it is imperative that power consumption (and consequently voltage per cell) be kept low, and the utilization of salt (and consequently the current efficiency) be kept high. Today, the industry occupies a very important position, as it concerns the production of not only caustic, chlorine, and bleaching powder, but also hydrochloric acid, hydrogen, sodium chlorate, and other chlorine products. Fig. 94 shows the trend of the reduction in the terminal voltage for the past three decades; Fig. 95

TABLE 127. United States Caustic and Chlorine Plant Capacity * (Installed or Building as of end of 1940).

#	Name	Location	Chlorine	Caustic Soda	Caustic Potash	Metallic Sodium	Magnesium	Soda Ash	Sodium Nitrate
1.	D. M. Bare Paper Co.	Roaring Springs, Pa.	1	1.1					
2.	Belle Alkali Co.	Belle, W. Va.	18	20.2					
3.	Brown Co.	Berlin, N. H.	36	40.6					
4.	Castanea Paper Co.	Johnsonburg, Pa.	11	12.8					
5.	Champion Paper & Fibre Corp	Canton, N. C.	32.7	36.8					
6.	Champion Paper & Fibre Corp.	Pasadena, Tex	20	22.5					
7.	Chemical Warfare Service	Edgewood, Md.	25	25					
8.	Chlorox Chemical Co.	Oakland, Calif.	4	4.4					
9.	Columbia Alkali Corp.	Barberton, Ohio	100	112.5					
10.	Diamond Alkali Co.	Painesville, Ohio	87	98.0					
11.	Dow Chemical Co.	Midland, Mich.	235	222.6			18		
12.	Dow Chemical Co. (Great Western Division)	Pittsburg, Calif.	69	76.4	2				
13.	Dow Chemical Co.	Freeport, Tex.	150	168.0			18		
14.	E. I. DuPont de Nemours & Co. (R. & H.)	Niagara Falls, N. Y.	100	13.5		65			
15.	E. I. DuPont de Nemours & Co.	Deepwater Point, N. J.	12						
16.	Eastern Mfg. Co.	South Brewer, Me.	6	6.7					
17.	Ethyl Gasoline Corp.	Baton Rouge, La.	83			55.1			
18.	Fields Point Mfg. Corp.	Providence, R. I.	7	7.8					
19.	Gulf Oil Corp.	Port Arthur, Tex.	15	16.8					
20.	Hercules Powder Co.	Hopewell, Va.	16	18.0					
21.	Hooker Electrochemical Co.	Niagara Falls, N. Y.	100	112.5					
22.	Hooker Electrochemical Co.	Tacoma, Wash	43	50.6	15				
23.	Isco Chemical Co.	Niagara Falls, N. Y	20	12.0					
24.	Jessup & Moore Paper Co.	Elkton, Md.	2.5	2.8					
25.	Kimberly-Clark Corp.	Kimberly, Wisc.	10	11.2					
26.	Matheson Alkali Works, Inc.	Niagara Falls, N. Y.	106	119.3					
27.	Michigan Alkali Co.	Wyandotte, Mich.	50	56.2					
28.	Monsanto Chemical Co.	Monsanto, Ill.	17	19.1	28				
29.	Niagara Alkali Co.	Niagara Falls, N. Y.	70	63.5					
30.	Niagara Smelting Corp.	Niagara Falls, N. Y.	20	22.5					
31.	Oxford Paper Co.	Rumford, Me.	12	13.5					
32.	Pennsylvania Salt Mfg. Co.	Tacoma, Wash.	35	39.4					
33.	Pennsylvania Salt Mfg. Co.	Wyandotte, Mich.	65	73.1					
34.	Penobscot Chemical Fibre Co.	Great Works, Me.	6	6.7					
35.	Ruggles & Rademacher	Manistee, Mich.	0.1	0.1					
36.	Solvay Process Co.	Baton Rouge, La.	42	47					
37.	Solvay Process Co.	Syracuse, N. Y.	65	61.1					120
38.	Southern Advance Bag & Paper Co.	Hodge, La.	12	13.5	22				
39.	Southern Alkali Corp.	Corpus Christi, Tex.	35	39.4					
40.	Texas Carbon Industries	Sayre, Okla.	1.25	1.4					
41.	S. D. Warren Co.	Cumberland Mills, Me.	8	9.0					
42.	Westvaco Chlorine Prod. Inc.	South Charleston, W. Va.	225	249.4	5				
43.	West Va. Pulp & Paper Co.	Covington, Va.	12						
44.	West Va. Pulp & Paper Co.	Luke, Md.	6					18	
45.	West Va. Pulp & Paper Co.	Mechanicsville, N. Y.	11	14.6				9	
46.	West Va. Pulp & Paper Co.	Tyrone, Pa.	6						
47.	West Va. Pulp & Paper Co.							9	
48.	Wm. Zinsser & Co.	New York, N. Y.	1.33	1.5					
	Total Daily Capacity		2,062.88	1,946.1	72	120.1	36	36	120
	Yearly Capacity (360 days)		742,636.80	700,596.0	25,920	43,230.1	12,960	12,960	43,200

* Cf. Murray, R. L., Growth of Electrolytic Alkali and Chlorine Industry in the U. S.—Development and Importance of Deposited Diaphragm Cell," Trans. Am. Inst. Chem. Engrs., 36, 445 (1940).

shows the improvement in the power and current efficiencies obtained during the same period.

Table 127 shows the total daily capacity of the alkali-chlorine plants in the United States as of November, 1940. Other products besides caustic soda and chlorine are also listed. This gives clearly the possibilities of the caustic soda and chlorine production annually in the United States by the electrolytic process.

Manufacture of Bleach. Chlorine gas from the anode compartments is conducted away in a 6-inch stoneware main and sent through the absorbing system (bleach towers) by means of a stoneware blower. The joints in the mains are luted with tar cement, which does not crack on being subjected to atmospheric changes. The main is provided with a U-tube manometer showing about $\frac{1}{16}$-inch water vacuum.

Chemically, as far as the solid bleaching powder is concerned, the bleach is not to be considered as a mixture of $Ca(ClO)_2$ and $CaCl_2$, but rather as a compound having the formula $Ca{<}^{ClO}_{Cl}.H_2O$ with a small excess of free CaO. There is evidence supporting this which cannot be discussed here. Pure $Ca(OH)_2$ would absorb chlorine to the extent of 43.5 per cent. Theoretically, according to the formula $Ca{<}^{OCl}_{Cl}.H_2O$, pure calcium hypochlorite should contain 49 per cent chlorine. But because of incomplete chlorination of the lime and decomposition of the hypochlorite, percentage of available chlorine is lower. The commercial basis, therefore, is 35 per cent bleach, meaning 35 per cent of its weight as available chlorine, although frequently the powder contains as high as 39 to 40 per cent available chlorine. Even the bleach liquor, which is rather dilute and is extensively used in paper and pulp mills, is referred to this 35 per cent basis. The lime used in making bleach must be high in CaO, and must contain less than 5 per cent $CaCO_3$ and 1 per cent of magnesia and silicious matter, and not more than traces of iron or manganese oxides.

For making bleach liquor the lime is slaked either by hand in slaking tanks, or in a continuous rotary slaker. The milk of lime must be allowed to cool before use.

$$CaO + Aq \rightarrow Ca(OH)_2 + Aq$$

The strength of the milk of lime depends upon the strength of the bleach required. For the bleaching of pulp in paper and pulp mills, where the strength of 60 grams of 35 per cent bleach per liter is generally required, milk of lime containing about 22 grams CaO per liter is employed. The lime solution is placed in a bleach tank provided with a stirrer. From the bottom of the tank, a pump sends the milk of lime to the top of the bleach towers whence it sprays down and runs over internal overflows, meeting chlorine gas entering from the bottom of the tower countercurrently. The tower is made of concrete, and has flat division plates and overflows arranged in a zig-zag way. This provides a long course for the flow of

milk of lime and an intimate contact with the chlorine gas sent in by a stoneware fan. The milk of lime flows from the bottom of the tower through a gas seal back to the bleach tank, from which it is again circulated by the pump through the towers until almost all the CaO is used up (leaving only 2 to 4 grams CaO per liter).

$$Ca(OH)_2 + Cl_2 \rightarrow Ca{<}^{OCl}_{Cl} . H_2O$$
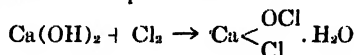
Milk of lime containing 35 pounds CaO will make a bleach liquor containing 100 pounds of 35 per cent bleach.

Usually two towers are used in series to insure complete absorption, and the spent gas is exhausted to the atmosphere. When one bleach tank is finished the agitation is stopped, and a new tank containing fresh milk of lime is cut in and circulated in the same way. The bleach liquor in the tank then is allowed to settle and the clear liquor drawn out through a syphon for use in the bleaching room. After all the clear liquor has been drawn out, the slime or "grout," containing an excess of lime, calcium carbonate, and silicious matter, is washed and strengthened with fresh milk of lime to the proper strength for a new batch. If lime is exhausted and the circulation of the bleach continued, there is a danger of losing the bleach.

$$H_2O + Cl_2 \rightarrow HClO + H^+ + Cl^-$$
$$2HClO \rightarrow 2H^+ + 2Cl^- + O_2$$
$$CaClO . Cl + H^+ + Cl^- \rightarrow Ca^{\cdot\cdot} + 2Cl + HClO$$

and

$$2HOCl \rightarrow 2H^+ + 2Cl^- + O_2$$
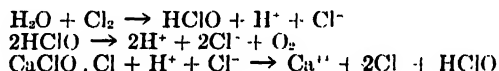
The liquor must be kept below 35° C., or decomposition of the bleach and conversion into chlorate is likely to occur.

If much $CaCO_3$ is present in the milk of lime, the acid is neutralized, and the bleach made is unstable, the hypochlorous acid formed being soon decomposed.

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$
$$2H^+ + 2Cl^- + CaCO_3 \rightarrow Ca^{\cdot\cdot} + 2Cl + CO_2 + H_2O$$
$$2HClO \rightarrow 2H^+ + 2Cl^- + O_2$$
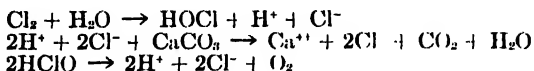
In both of the following reactions:

$$Cl_2 + H_2O \rightleftarrows H^\cdot + Cl^- + HClO$$
$$HClO \rightleftarrows H^+ + ClO^-$$
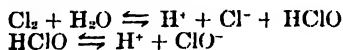
a decrease in pH value, *i.e.*, the addition of a mineral acid, would push the reactions from right to left; whereas an increase in pH by the addition of an alkali would cause them to proceed from left to right. In the latter case the following equilibrium is established:

$$ClO^- + H_2O \rightleftarrows OH^- + HClO$$
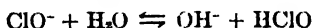
The presence of magnesia in the lime will cause the bleach to be decomposed rather quickly. The maximum amount of magnesia in the lime should not exceed 2 per cent.

The presence of iron or manganese oxides in the bleach liquor causes

rapid decomposition of the bleach, so that the lime used should contain very little of these oxides.

$$2CaClO \cdot Cl \rightarrow 2Ca^{++} + 4Cl^- + O_2 \text{ in presence of iron or manganese oxides.}$$
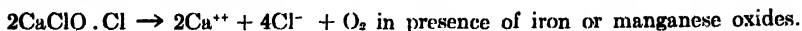
For a strong bleach solution containing 250 grams or more of 35 per cent bleach per liter, normal strength of milk of lime is used in the beginning, but more lime can be added as absorption proceeds. The process of chlorination thins down the suspension so that the addition of more lime later does not affect the flow through the towers. Care must be taken to keep the solution cold (about 20° C.); otherwise the bleach will not settle well and may be chlorated to an excessive extent:

$$6CaOCl \cdot Cl \rightarrow 5Ca^{++} + 10Cl^- + Ca(ClO_3)_2$$
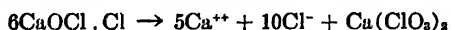
Sometimes, the cell effluent itself is used to absorb chlorine in making bleach liquor, but this is very wasteful.

Manufacture of Bleaching Powder. For making bleaching powder, an absorption apparatus known as the Hasenclever's mechanical chambers is used, consisting of 6 to 8 sections of lead-lined cast-iron screw mixers, 20 inches in diameter and about 12 feet long, placed one on top of another and driven by a system of cog-wheels so that the slaked lime travels down from the top in a zig-zag way until it reaches the bottom tier, where it is discharged out as bleaching powder. Dried chlorine gas diluted with air is blown in from the bottom and the spent gas let out from the top countercurrently. The quicklime for this purpose must contain high CaO and very small quantities of iron or manganese oxides, as mentioned before. Further, it must be slaked with enough water so that there is present about 4 per cent free moisture in the $Ca(OH)_2$ formed, or about 28 per cent total water on the weight of the hydrated lime. The screw consists of a shaft with a number of spiral spuds attached to it, the spuds scraping the lime as well as pushing it along. Any two adjacent sections one above the other have the spiral spud shafts turned in opposite directions from the motion of the spur gear wheels in direct gearing. Slaked lime sifted through a screen enters from a hopper on the top. Considerable heat is generated during chlorination, and it is necessary to keep the temperature below 40° C. and to run intermittently. On this account, dilute chlorine gas is preferable. It is a good plan to run a slightly higher vacuum on the chlorine main, as much as $\frac{1}{3}$ inch of water. This serves to dilute the gas and at the same time keep the loss to a minimum. Excess of free CaO in bleaching powder runs about 10 per cent. The finished product is packed in steel drums weighing from 300 to 400 pounds net.

A newer type of mechanical chlorinator is based on the same principle as the Herreshoff or Wedge burner. There are about ten shelves with a 5- to 6-inch C.I. pipe shaft carrying scraping arms which are provided with malleable cast-iron rabbles to scrape the lime from one shelf down to another, first through the central opening and then the side opening in the periphery of the shelf in a zig-zag way. Chlorine gas is led in through the bottom and the lime is charged from the top. The shelves are made

of concrete with cooling water pipes embedded therein, both for cooling and for reinforcement. The circular body of the chlorinator is also made of reinforced concrete.

Formerly, large stationary bleach chambers were used, four of these being connected in series. The chambers were lead-lined concrete structures with asphalt-covered flooring, and were cooled by cooling coils located under the floor surface. Chlorine gas was passed through these chambers in series and absorbed by lime on the floor. The lime was introduced from hoppers located on the roof and spread over the floor by hand. When the desired strength was reached, the remaining chlorine gas was exhausted from the head chamber to a secondary lime chamber. Men went in to rake the bleaching powder and clear it out. A new batch of lime was then put in and this chamber made the tail end of the series. The conditions were rather hard on the workmen. A gas mask should be provided for each man working inside.

Manufacture of Liquid Chlorine. Instead of making bleaching powder, large quantities of chlorine are now liquefied as liquid chlorine and sold to the textile manufacturers. For this purpose, the gas is kept as rich as possible by avoiding air leakages and excessive vacuum in the main. The gas is first dried in two stoneware towers in series using 93 per cent sulfuric acid as the drying medium. The gas is pulled through these towers by means of Nash "Hytor" pumps using 93 per cent acid as seal in the casing. The pumps, which are made of cast iron, are not attacked by the dry chlorine gas or the strong sulfuric acid. Each pump can develop a pressure of 25 to 50 pounds and thus keep the gas under this pressure in the refrigerating system, using brine at a temperature of about 10° F. Sometimes two such pumps are used in series. Chlorine under this pressure and temperature is liquefied and the dried liquid chlorine is safely handled in steel cylinders of 100 to 150 pounds or of one ton net weight, or in tank cars containing 16 tons net. Liquid chlorine is now handled in the trade in place of bleaching powder. From it the bleach liquor can be conveniently made in the consumer's own plant by bubbling chlorine gas through a soda ash solution of suitable strength to form sodium hypochlorite bleach liquors. It is thus in a concentrated form ready for use and may be prepared whenever it is needed.

Manufacture of Synthetic Hydrochloric Acid. At present large amounts of chlorine are also used in the manufacture of concentrated hydrochloric acid. For this purpose, the hydrogen gas and the chlorine gas from the cell room are brought in two separate pipes in suitable proportions under slight pressure into a vertical brick-lined cylinder or horizontal brick furnace, where they are burned.

$$H_2(gas) + Cl_2(gas) \rightarrow 2HCl(gas) + 44,000. \quad Q = 22,000 \text{ cal./mol HCl}$$
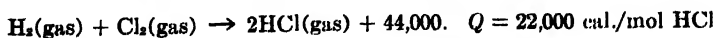
Considerable heat is developed but it is usually not utilized. The hydrogen chloride gas must be cooled in silica and stoneware pipes and absorbed in water to form concentrated hydrochloric acid in Cellarius tourills and acid-proof towers.

With the production of chlorine, the variety of products in the alkali plants is further multiplied. Alkali manufacturers are now manufacturing many chlorine derivatives such as mono-chlorobenzene (from the reaction of chlorine gas on benzene), para- and ortho-dichlorobenzene, potassium chlorate, sulfur monochloride (from the direct union of chlorine gas and sulfur), etc. These products should be added to the list enumerated in Chapters XV and XVI.

Evaporation of Caustic Liquor. The cell effluent is collected in weak liquor storage tanks, from which it is pumped to evaporators for concentration. Zaremba, Buffalo Foundry, or Swenson evaporators of the submerged vertical tube type with salt catchers attached or with continuous salt separators, are among the ones most generally used. Two effects (and sometimes three) are generally arranged. According to the practice of one plant, each evaporator is 80 inches in diameter and 12 feet high, holding about 1000 gallons of the liquor. In the first effect, exhaust steam, or live steam throttled to 25 lbs. pressure, is employed, and the pressure above the liquor in the first effect varies from 5 lbs. pressure to 3 lbs. vacuum. The liquor is sucked over to the second effect by vacuum and so to the third (if any). The vacuum above the liquor in the last effect is from 26 to 27 inches Hg. Condensed steam from both effects goes to the boiler. The condensate from the first effect is forced by its own pressure to the boiler feed tank, but that from the second (and the third) requires a pump. On the top of the second effect (or last effect) is located a cyclone separator, to the outlet of which a barometric condenser is attached. This may be a countercurrent type with steam from the last effect coming into the bottom of the condenser and the water entering at the top, flowing over zig-zag baffle plates. The vacuum may be created by means of a steam ejector (using 60 lb. or higher steam pressure), or by means of a dry-and-wet pump. This vacuum connection is located on the crown of the condenser. In the second (or last) effect the caustic liquor is concentrated to about 47° Bé. and the concentrated liquor is drawn off and allowed to settle in tall tanks where most of the salt separates out. The analysis of the strong caustic from the evaporator is given in Table 128.

TABLE 128. The Strong Caustic from Evaporator.

	Before Settling	After Settling
Sp. gr. at 25° C.	1.475 (47° Bé.)	1.475
NaOH	628 grams per liter	628
NaCl	47.2 " " "	10.7
Na₂SO₄	3.0 " " "	0.4

It will be seen that considerable sodium chloride and sulfate will have separated out from the strong caustic inside the evaporators. The strong caustic after complete settling is now a commodity on the market known as liquid caustic.

Caustic made this way will contain considerable NaCl as the main impurity which may be objectionable in certain industries, such as the rayon industry. One method of manufacturing NaCl-free caustic is to

bring the caustic liquor to 47° Bé. and settle off sodium chloride as much as possible, as described above. The clear liquor then is diluted down to about 37° Bé. and cooled to about 35° F. when crystals of NaOH . 3½H₂O or NaOH . 4H₂O separate out, leaving NaCl in the mother liquor. These crystals almost free from NaCl are filtered off and melted and the solution is concentrated back as usual.

As the 47° Bé. caustic concentrated from the cell liquor is saturated with respect to NaCl, it may still contain 2.2 g NaCl and 0.08 g Na₂SO₄ per 100 g Na₂O, after complete settling. Even the fused caustic obtained from this would contain 0.7 g NaCl per 100 g Na₂O. It is therefore desirable to get rid of the excess NaCl in the electrolytic caustic. D. A. Pritchard * proposed to treat the 47° Bé. electrolytic caustic liquor by adding to the liquor finely pulverized anhydrous sodium sulfate in an amount 3-4 times the weight of NaCl present, heating and stirring so as to form a triple salt of NaCl, Na₂SO₄ and NaOH, which will separate on cooling and settling. It is claimed that in this way the resulting caustic contains as low as 0.2 g NaCl per 100 g Na₂O.

If solid caustic is desired, this clarified 47° Bé. caustic is decanted and further concentrated in cast-iron open pots by direct heat for 3 to 4 days. The molten caustic is then pumped by means of a centrifugal pump made of pure nickel or ladled to steel drums, as explained in Chapter XIX.

The salt from the catchers is washed until it contains only 0.1 per cent sodium hydroxide, when it is dissolved with warm water and the solution used for treating raw brine in conjunction with the soda ash treatment mentioned at the beginning of the chapter. The wash water is sent back to the evaporators with the weak liquor. When these sodium chloride and sodium sulfate crystals are dissolved and sent back to the raw brine-treating tanks it is easily seen that sodium sulfate will accumulate in the brine, causing low efficiency in the cells and much oxygen gas generated at the anodes. To get rid of sodium sulfate, barium chloride solution may be employed when necessary.

As the evaporators are frequently made of steel, any hypochlorite carried in the weak liquor (or cell effluent) would attack the steel material very rapidly, causing corrosion in the steam chest and leaks in the tubes. It cannot be too strongly emphasized that every effort must be made to keep the cell effluent free from hypochlorite, or the upkeep on the evaporator will be heavy. If proper attention is given to the operation of the cells, these tubes should last for more than two years. Nowadays these evaparator tubes are frequently made of pure nickel, giving a product of the purity required by the rayon manufacturers. Such nickel-tube evaporators will take higher steam pressures and with forced circulation can concentrate the liquor to 74 per cent NaOH or higher. Nickel-tube evaporators permit the use of higher steam pressure, with consequent higher concentration of the caustic; for then there is no danger of caustic embrittlement, as would be the case in the steel tube evaporators when a high steam pressure is used.

* B. P. 299,995 (1928).

One manufacturer in the United States uses caustic evaporators made entirely of nickel—body, tubes and all. This nickel equipment, coupled with vigilant care in selecting high-grade raw materials and in keeping all impurities, both metallic or of alkaline-earth origin, away from contact with the weak liquor in the course of manufacture both prior and subsequent to this evaporation process, insures a pure product that will meet any requirements demanded of the liquid caustic. In this way, recrystallization of the caustic as above mentioned is no longer necessary.

Manufacture of Sodium Chlorate. The manufacture of sodium chlorate is done by electrolytic methods using cylindrical cells somewhat like Vorce cells, or rectangular type cells. The cells use graphite electrodes and iron cathodes, as in the alkali-chlorine cells, but without asbestos diaphragm. The brine used, too, is saturated and must be free from calcium, magnesium, sulfates, and iron. Here similarity 'ends, for to the brine in the cells must be added hydrochloric acid to maintain an acidity of pH 6.4-6.6 so as to bring about the oxidation of $NaClO_3$ by the hypochlorous acid in the cell; also sodium dichromate must be added to protect the iron cathode from the action of hypochlorous and hydrochloric acids. Calcium and magnesium must be absent from the cell liquor; otherwise these would be deposited on the cathode, causing high voltage drop at the cathode surface. Sulfate must be kept within a very low limit because $SO_4^{=}$ ions would carry current to the anode, liberating oxygen, oxidizing the anode and causing losses of graphite. Iron must be absent in order that hypochlorous acid and sodium hypochlorite may be stable, cathodic reduction reduced, and current efficiency improved.

A cylindrical cell [*] 33 inches in diameter and 4 feet high will take 1300 to 1500 amp. per cell at a voltage per cell from 2.8 volts to 3.6 volts, depending upon the current density, when using 2″ by 2″ (or 2″ round) by 36″ long (overall) graphite anodes, although the theoretical voltage is only 1.5 volts. The current density is about .04-.06 amp. per sq. cm. and the current concentration (*i.e.*, amp. per liter of cell liquor) is 4.0-5.0. Cooling of the cell liquor is necessary; this may be accomplished by internal cooling using either cooling coils as a part of the cathode in the cell, or outside cooling by circulating cell liquor through outside coils made of iron pipes cathodically protected. The cell liquor temperature is approximately 25-30° C., depending upon the cooling surface provided and cooling water temperature available. High cell liquor temperature would cause excessive graphite losses. A cell operating at 42° C., for instance, will have anode losses about double that at 32° C., and a cell operating at 32° C. again double that at 25° C.

The reactions are as follows:

(1) $6NaCl + 6H_2O + 6 \text{ faradays} \rightarrow 6NaOH + 3H_2 + 3Cl_2$
(2) $2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$

[*] Cf. Groggins, Pitman, McLaren and Davis. "Electrochemical Production of Sodium Chlorate," *Chem. Met. Eng.*, June, 1937; Pitman, McLaren, Davis and Groggins, "Sodium Chlorate Production," *ibid.*, December, 1938; also Groggins, Pitman, and Davis, "Sodium Chlorate Cell Design," *ibid.*, July, 1940.

(3) $2Cl_2 + 2H_2O \rightarrow 2HOCl + 2HCl$
(4) $NaOCl + 2HOCl \rightarrow NaClO_3 + 2HCl$
(5) $4NaOH + 4HCl \rightarrow 4NaCl + 4H_2O$
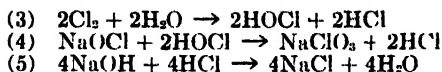
Adding these five equations we obtain

(6) $NaCl + 3H_2O + 6 \text{ faradays} \rightarrow NaClO_3 + 3H_2$

and from the thermochemical equation

$$NaCl + 3H_2O \rightarrow NaClO_3 + 3H_2 + Q$$
$$(-96,400) \quad (-3 \times 68,370) \quad (-81,100)$$
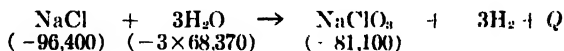
we estimate roughly

$$E = \frac{220,400 \times 4.187}{6 \times 96,540} = 1.59 \text{ volts}$$

If we take account of the temperature-coefficient term, the theoretical decomposition voltage is 1.50. But actually with the space of $\frac{3}{4}$ inch between the graphite anodes and the iron cathode and with a current density of 0.3 amp. per sq. in., the terminal voltage is 3.3 volts. Thus, the overvoltage due to polarization, etc. is very high. The current efficiency is about 83 per cent because of many secondary reactions, while the power efficiency is below 40 per cent. The anode consumption is a big item of expense. Denser graphite of sp. gr. 1.7 or higher lasts longer.

The brine entering the cells contains about 350 g/l NaCl and 2 g/l Na_2CrO_4 and the cell effluent contains 550 g/l $NaClO_3$ and 60-80 g/l unconverted salt. It is possible to operate four to eight of such cells in series (chemically), transferring the liquor by syphon or gravity from the first cell in the series to the next. In this way, it is possible to get low unconverted NaCl and high $NaClO_3$ concentration and operate the cells continuously, feeding the brine at the head cell of the series and drawing the effluent from the last cell in the series. To avoid grounding of the current, a device is used to feed brine into the cell in drops or in a discontinuous stream (see Fig. 96). Hydrochloric acid may be added to each cell in the series (to the immediate cells as well as the head cells) and the pH value of each cell carefully regulated.

A rod-cathode cell * construction is found to possess a much higher efficiency than the ordinary plate-cathode cell above described. Such a rod-cathode assembly (Fig. 97) with a single 2-inch diameter central graphite anode surrounded by ten $\frac{1}{4}$-inch diameter steel cathode rods, equally spaced around a circle of $2\frac{3}{4}$ inches diameter, at a distance of about $\frac{3}{8}$ inch from the center of the rods to the surface of the anode, has a much higher current efficiency and a lower terminal voltage. This type of cell has less resistance because of shorter distance between the cathode and anode surfaces ($\frac{1}{4}$ inch) and hence a lower terminal voltage (2.8-3.2 volts), and has a more efficient stirring effect so that a current efficiency of 93 per cent is obtainable with higher current density (.05-.06 amp. per sq. cm.) and

* Cf. a very recent article by James McLaren, etc. entitled "The Efficiency of a Sodium Chlorate Cell with Rod Cathodes," *Trans. Elec. Chem. Soc.*, **79**, for April meeting, 1941.

current concentration. The energy required is about 2.4 kw-hr. per lb. of sodium chlorate made. A single unit of this rod-cathode assembly, 2 feet 6 inches long, will carry 100-150 amp. of current so that a number of such units may be conveniently placed in a cell and connected in parallel for a large capacity. The capacity of each cell is then directly proportional to the number of such units it contains. Thus, a very compact arrangement is obtained for a large capacity cell. A number of such cells are then connected in series for operation as usual.
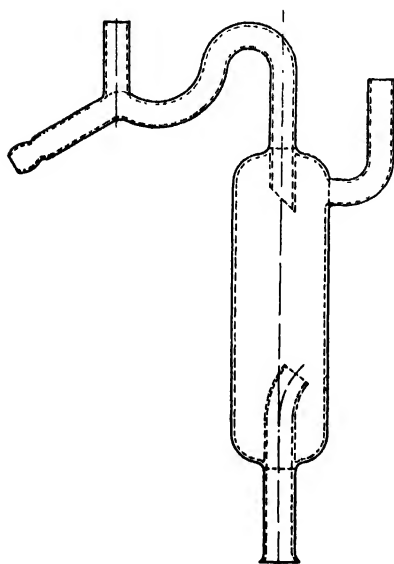
FIG. 96. Glass brine feeder.
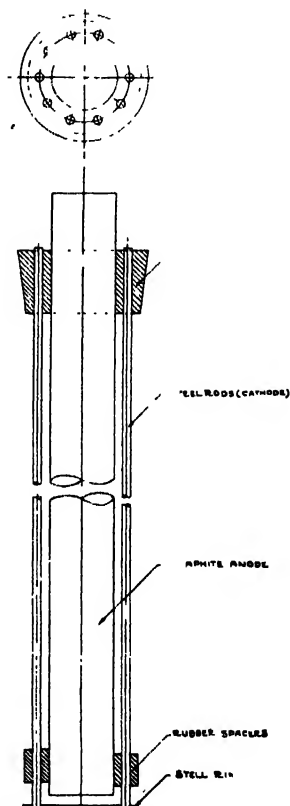
FIG. 97. Rod-cathode cell assembly.

The rod-cathode cell tank may be made of earthenware, concrete, or even steel plate. If made of concrete, it should be coated inside with a coal-tar protective paint or with Chinese wood oil or linseed oil to preserve the concrete surface from crumbling. The upper part of each graphite anode may be impregnated with paraffin to prevent diffusion of chlorine through the porous graphite. The top of each anode, where electrical contact is made, is best copper-plated to secure good electrical contact. Care should be taken not to copper-plate lower portion of the anode that

may come into contact with the cell liquor; otherwise the anode would deteriorate rapidly due to local cell action. The cell cover may be made of 1-inch asbestos "Ebony" or "Chemstone" board of Johns-Manville make. Joints around the edge of the cover may be sealed with water glass or rubber cement, or with any other inert plastics. One such composition is prepared by melting together

Rosin	75 pts by wt.
Gum rubber	15 " " "
Beeswax or other wax	10 " " "

and adding to the melt a small quantity of fine asbestos fiber. The proportion of rosin to wax may be varied according to the consistency desired.

Also, it is found that in the rod-cathode cell if the sulfate ions (SO_4^{--}) are kept out of the cell liquor, the cell will operate with almost no chromate. Then the anode life is very much lengthened, while the cathode reduction is not increased. It seems that while sodium chromate protects the cathode surface, it has a tendency decidedly to accelerate oxidation of the graphite anodes.

Electrometric measurement of the pH values must be employed if accurate results are desired, because the pH Comparator is rendered useless on account of the presence of strongly oxidizing hydrochlorous acid, which would destroy the indicator in the solution, and because the solution is highly colored. The color range of $CrO_4^= \rightleftarrows Cr_2O_7^=$, however, may be used as a rough guide in the field for comparison against a series of known standards. The cell effluent is collected in a glass-lined settling tank where the graphite slime is allowed to settle off and time is allowed to complete the reaction between sodium hypochlorite and hypochlorous acid.

$$NaClO + 2HClO \rightarrow NaClO_3 + 2HCl$$
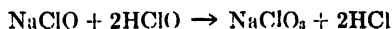
Acidity in the liquor here is constantly adjusted so that enough hypochlorous acid is liberated for the oxidation of sodium hypochlorite to chlorate.

$$2HCl + 2NaClO \rightarrow 2NaCl + 2HClO$$
$$2HClO + NaClO \rightarrow NaClO_3 + 2HCl$$

The following reaction

$$HClO + 2Cl_2 + 2H_2O \rightarrow HClO_3 + 4H^+ + 4Cl^-$$
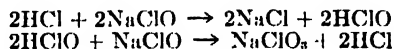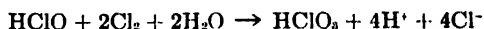
increases the acidity and causes the lowering of pH in the liquor as the reaction proceeds. This conversion of HClO to $HClO_3$ is arrested if the pH of the solution falls below 2 (for then most chlorine would exist as Cl_2); and again, if the pH increases beyond 9 (for then chlorine would exist mostly as ClO^- ion). Between the pH values of 2 and 9, this conversion proceeds favorably, the optimum being at pH = 5, for then the concentration of HClO is at a maximum. Table 129 shows the ratios of HClO to ClO^- and Cl_2 to HClO at different pH values at 25° C.

When the reaction is complete, the liquor is neutralized with caustic soda or soda ash and passed through a sand filter to remove the residual

TABLE 129. Relative Composition of Cl_2 Solution at Various pH Values.*

pH	Ratio HClO to ClO⁻		Ratio Cl_2 to HClO
	Sand	Soper	Jakowkin
1	2.3×10^6	10^7	30
2	2.3×10^5	10^6	1
3	2.3×10^4	10^5	1/13
4	2.3×10^3	10^4	1/130
5	2.3×10^2	10^3	1/1330
6	2.3×10	10^2	
7	2.3	10	
8	1/4	1	
9	1/44	10^{-1}	
10	1/440	10^{-2}	
11	1/4440	10^{-3}	
12	1/44400	10^{-4}	
13	1/440000	10^{-5}	

* Rue, John D., "The Chemistry of Bleaching Chemical Wood Pulps," *Trans. Electrochem. Soc.*, Paper Presented to Savannah' Meeting, May (1938). Figures taken from "Die Bleiche des Zellstoffs," I, p. 77 (1935).

graphite slime. Neutralization is performed to destroy the acidity, so that the liquor may be concentrated in evaporators for the recovery of $NaClO_3$ crystals. This separation of $NaClO_3$ crystals from the liquor may be accomplished by (a) evaporating the liquor in vacuum evaporators and cooling the concentrated liquor so as to throw out $NaClO_3$, or (b) by salting out the $NaClO_3$ crystals in the liquor with solid salt in finely pulverized form to obtain saturation with respect to NaCl and cooling the liquor to a low temperature, say 15° C., to crystallize out $NaClO_3$. $NaClO_3$ crystals which appear yellowish because of the presence of a small amount of sodium dichromate, are dried in a centrifuge and washed with a small amount of water on the centrifuge to obtain white color. The mother liquor is reconcentrated and eventually returned to the cells for the preparation of brine for electrolysis. The sodium chlorate crystals are dried in a hot-air shelf dryer at 140-160° F., heated by low-pressure steam (10-15 lbs. gauge) coils, and then packed in paper-lined, hermetically-sealed, tinned containers holding 100 lbs. each.

In the operation of the chlorate cells, it is very important to regulate the pH values in the cells and also in the settling tanks where the oxidation of sodium hypochlorite to chlorate is allowed to be completed, while the graphite slimes are being separated. After completion of the reaction, the liquor is heated by steam jacket and agitated by compressed air to destroy excess hypochlorous acid. Decomposition of the hypochlorous acid is aided by heat and aeration. Neutralization is then effected by the use of soda ash or caustic soda, so that this neutralized liquor devoid of hypochlorous acid may be concentrated in cast-iron or alloyed cast-iron (austenitic cast iron containing small amounts of nickel or chromium) evaporators at an elevated temperature without excessive corrosion. It is, however, more advisable to use stainless steel or copper evaporators for this purpose.

The liquor foams badly in the evaporators, but this trouble may be minimized by making the liquor distinctly acid before heating and agi-

tating to destroy the hypochlorite in the settling tank mentioned above.

The mother liquor from the crystallizer and the centrifuge may be returned to the evaporators for further concentration and a portion of it may be sent to the makeup tank for feeding into the cells, thus returning the sodium chromate to the cell liquor. Care must be taken to avoid accumulation of metallic impurities—iron oxide particularly—in the liquor. The effect of iron rust in the cells is to cause excessive losses by reduction, thereby lowering the current efficiency. Consequently, the concentration of iron in the cell liquor must be carefully watched, and the iron oxide formed in the cells must be allowed to settle quietly to the bottom of the cell and not to be circulated with the liquor stream.

Sodium chlorate is used for killing the weeds in the farms and may be mixed with TNT or nitroglycerine for the manufacture of detonators.

Manufacture of Potassium Chlorate. The manufacture of potassium chlorate is not carried out by electrolyzing potassium chloride (KCl) in the cells, as might be inferred from sodium chlorate manufacture, because potassium chlorate is difficultly soluble. Instead, sodium chloride is used to make sodium chlorate liquor as described above. The cell effluent is then taken and treated with finely pulverized potassium chloride, thereby causing potassium chlorate to be formed by metathesis:

$$NaClO_3 + KCl \rightarrow KClO_3 + NaCl$$
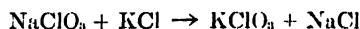
Potassium chlorate, being less soluble, separates from the liquor. The mother liquor is then returned to the cell for the preparation of the brine for electrolysis. Thus, the process does not call for concentrating the cell liquor by evaporation.

Potassium chlorate is used in the manufacture of matches and in the munitions industry.

Chapter XXI

Wet Calcination of Sodium Bicarbonate

Decomposition of crude sodium bicarbonate, or ammonia soda, into soda ash is normally done in a dryer with external firing. "Wet calcination" is a term applied to the operation of decomposing sodium bicarbonate into soda ash in the wet way in contradistinction to dry calcination. Wet calcination is advantageous when soda ash is to be used in the form of a solution for the subsequent manufacturing processes, $i.e.$, when it would have to be dissolved in water for further application. With steam as the source of heat instead of direct firing, wet calcination has the advantage over dry calcination by means of a dryer, because it has a better over-all heat efficiency and because the operation is simpler and does not entail such mechanical difficulties as are ordinarily encountered in an externally fired furnace, especially when the crude bicarbonate obtained is wet and the crystals are poor and in the form of a fine sludge. Further, it enables caustic soda to be manufactured directly from sodium bicarbonate instead of from soda ash, into which sodium bicarbonate would have to be first dried and calcined, and from which a solution then would have to be made. And it is even more feasible to recover CO_2 gas from decomposition by wet calcination in a very rich form—in fact approaching 100 per cent CO_2.

Decomposition of sodium bicarbonate by either dry or wet calcination is endothermic, and the heat in the wet calcination operation comes from steam. In wet calcination it takes heat to dissolve sodium bicarbonate, to heat up the solution and to drive off CO_2 from the solution. Theoretically, the quantity of heat required per kg. mol of $NaHCO_3$ may be estimated from the following thermochemical equation:

$$2NaHCO_3 \text{ (diss.)} = Na_2CO_3 \text{ (diss.)} + H_2O \text{ (liq.)} + CO_2 \text{ (sat.)} + Q$$
$$(-2 \times 225,000) = (-278,200) + (-68,370) + (-103,680) + Q$$
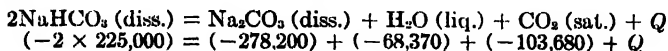
Q equals -250 kg. Cal. for 2 kg. mols $NaHCO_3$, a very small figure or practically nil; $i.e.$, the above reaction, starting from sodium bicarbonate in solution and ending in soda ash and CO_2 in solution, has practically zero heat effect. Therefore, not only does wet calcination provide better heat transfer, but the quantity of heat required is actually smaller, because Na_2CO_3 is obtained in solution and H_2O in the liquid form. Heat, however, is required to dissolve solid sodium bicarbonate (heat of solution), to heat up the solution, and to drive CO_2 out of solution. Moreover, the steam used serves a twofold purpose: (1) to furnish the heat necessary for decomposition, and (2) to act as a distilling medium lowering the partial pressure of CO_2 above the solution. In this way, the partial pressure

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of CO_2 at the bottom of the decomposer is reduced to a very low figure, less than 0.01 atm. Generally speaking, the bicarbonate slurry contains about 4.5 normals total sodium, and the slurry goes into solution completely toward the end of decomposition. From the equilibrium relationship derived by Harte, Baker and Purcell (see p. 278), taking the boiling temperature of only 100° C. and the partial pressure of CO_2 at 0.01 atm. at the bottom of the decomposer, we have

$$\frac{x^2 C^{1.25}}{1-x} = 10 SP (185 - t),$$

$$\frac{x^2}{1-x} \quad \frac{10 \times .0065 \times .01 (185 - 100)}{(4.5)^{1.25}}$$

$$x = 8.5\%$$

Bicarbonate decomposer.
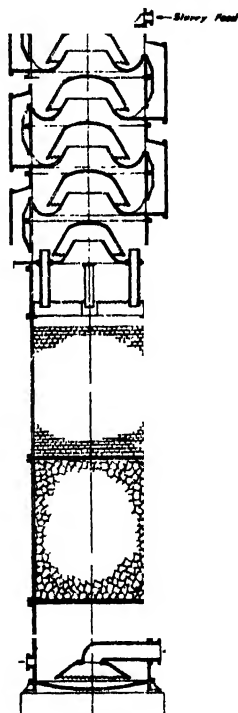
That is, the bicarbonate under such conditions could be decomposed to 91.5 per cent soda ash. But in practice, because of the length of time it takes to reach the equilibrium and the excessive steam required, decom-

position generally stops at around 85-87 per cent at the exit from the decomposer, and sometimes less.

A decomposer is very similar to a distiller in its operation. It is a CO_2 stripping column with rectification for CO_2 gas, all arranged countercurrently. While a distiller distills off ammonia, a decomposer distills off CO_2 gas. The steam used in the decomposer is generally low-pressure steam of 6-10 lb. per sq. in. gauge, but may be 60-lb. pressure steam. One type of decomposer is shown in Fig. 98. The bicarbonate slurry containing about 4.5 normals of sodium is fed to the bubble-cap portion on the top, trickling through packed sections to the bottom, where steam is introduced countercurrently as in a distiller. CO_2 gas from the decomposition, saturated with steam, leaves the top of the decomposer, passes through a condenser to condense out as much steam as possible, and is finally cooled on its way to the compressor intake main. This cooled gas will contain 95 per cent CO_2 by volume or more, if the system is reasonably tight. The slurry is made up of various returned liquors, weak wash liquor or condensate, to which crude sodium bicarbonate or any rejected soda is added, and the suspension is kept at about 50° C. The crude sodium bicarbonate contains, besides $NaHCO_3$, small quantities of NH_4HCO_3, $NaCl$, Na_2CO_3 and NH_4Cl. The reactions in the decomposer are:

(1) $NH_4HCO_3 \rightarrow NH_3 + CO_2 + H_2O$

(2) $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

(3) $NH_4Cl + NaHCO_3 \rightarrow NaCl + NH_3 + CO_2 + H_2O$
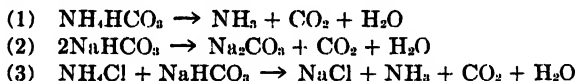
NH_3 and CO_2 are distilled off, but all the NaCl remains in the decomposed liquor. Indeed, these reactions are very similar to those occurring in the ammonia distiller, except that no lime is introduced. But whereas in the distiller operation, exhaust steam of 6-10 lb. gauge is generally used, in the decomposers the steam pressure may be as high as 60-lb. gauge, to give more rapid and complete decomposition, especially if the decomposed liquor is to be causticized for caustic soda manufacture.

From the equation referred to above

$$\frac{x^2}{1-x} = \frac{10SP\,(185-t)}{C^{1.29}}$$

where x represents the degree of bicarbonation (fraction as $NaHCO_3$), it will be seen that a higher steam pressure (consequently a higher steam temperature) has several advantages, because

(a) solubility of CO_2 gas in the liquor is decreased with the increase in temperature;

(b) increase in temperature gives a smaller value of x;

(c) the rate of decomposition is increased as the temperature is increased, it being doubled for every 22-24° C. temperature rise;*

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* Whitman, W. G., and Davis, G. H. B., "A Comparison of Gas Absorption and Rectification," *Ind. Eng. Chem.*, **18**, 264 (1926).

Harte, C. R., and Baker. E. M.. "Absorption of Carbon Dioxide in Aqueous Sodium Carbonate-Bicarbonate Solutions," *ibid.*, **25**, 1128 (1933).

(d) increase in steam pressure and temperature causes less condensation and gives greater steam-distillation effect in the decomposer.

The CO_2 gas from the decomposer, after passing through a condenser and cooler, is usually sent to the rich CO_2 main at the intake to the CO_2 compressors to be delivered to the "making" columns for ammonia soda manufacture; but if 60-lb. steam is used, it is also possible to conduct the rich gas from the decomposer directly to the bottom of the "making" columns by means of a constant-volume distribution control without going through the CO_2 compressors. .

Wet calcination may be used to advantage in the following processes where crude bicarbonate is used directly—all in the form of a solution:

(a) the manufacture of sodium sesquicarbonate;
(b) the manufacture of refined sodium bicarbonate;
(c) the manufacture of caustic soda.

Practically the same design of decomposer may be used for all three purposes, but the control may be different as regards the slurry concentration, the degree of decomposition, and the optimum steam pressure for the decomposer, all of which may vary in accordance with the purpose for which the decomposed liquor is to be used. Frequently, certain alkali rejects are used together with the bicarbonate to make the slurry for their alkali value. These may be soda dust from dust collectors, fines from dense ash screening operation, off-color ash from the starting-up of a new apparatus, floor sweepings, etc. which are first dissolved and then settled and decanted before they are added to the bicarbonate.

Unlike the distiller operation, the decomposer operation is rather simple, there being less tendency for the formation of scales or the deposition of insoluble sludge. Hence, as pointed out above, a higher steam pressure is more commonly used in the decomposer than in the ammonia distillers. In general, also, plain-steel plates are frequently used for the construction of the decomposer instead of the cast-iron rings which are more generally employed for the distiller, especially for the upper sections above the lime inlet.

The Manufacture of Sesquicarbonate. In the manufacture of the sesquicarbonate, the slurry used consists of about 520 parts of crude sodium bicarbonate to 1000 parts by weight of return water. The decomposition is carried up to about 78 per cent, *i.e.*, when 78 per cent of the bicarbonate has been converted to soda ash. The blow-off is then taken to a crystallizing tank and slowly cooled to allow needle-shaped (monoclinic), lustrous crystals of sodium sesquicarbonate, $Na_2CO_3 . NaHCO_3 . 2H_2O$, to form. Attention is given to controlling the operation so that all ammonia is driven out of the solution. At the end of the decomposition all bicarbonate should have gone into solution. The decomposed liquor is so concentrated that it may freeze in the pipes unless they are lagged. The following represents a typical condition of operation:

TABLE 130. Composition of Slurry for Sesquicarbonate Manufacture.

Slurry	520 kg. NaHCO₃ on dry basis per 1000 kg. return water
Total titer	114
Na₂CO₃ titer	89
NaHCO₃ titer	25
NaCl titer	1.0
Per cent decomposition	78
Bottom pressure	9 lb. gauge
Top temperature	88° C.
Top pressure	1.5 lb. gauge

The Manufacture of Refined Sodium Bicarbonate. The crude bicarbonate (ammonia soda) is suspended in the return liquor so that the slurry contains 480 kg. of the bicarbonate per 1000 kg. of water. The decomposition is carried to about 76 per cent using a moderate-pressure steam. At the end of decomposition, all the bicarbonate should have gone into solution at the temperature of the decomposer, and ammonia should have been completely distilled off. The liquor, however, is so concentrated that all pipes and storage tanks should be carefully lagged or traced with steam coils to prevent freezing. Decomposition is carried to the above extent in order to decompose all ammonium bicarbonate and drive out ammonia; but further decomposition is unwise, because the liquor has to be re-carbonated in the bicarbonate towers for the precipitation of sodium bicarbonate. For this purpose, lean gas (kiln gas) is used, which is pumped into the bicarbonate towers by means of the CO_2 compressors in the same way as in ammonia soda manufacture. The decomposed liquor is rapidly carbonated and cooled in the bicarbonate tower and the slurry is drawn out at the bottom and centrifuged. For details of the operation and the drying of the refined sodium bicarbonate, the readers are referred to Chapter XVIII. The following represent a typical condition of operation:

TABLE 131. Composition of Slurry for Sodium Bicarbonate Manufacture.

Slurry	480 kg. bicarbonate on dry basis per 1000 kg. return liquor
Total titer	106
Na₂CO₃ titer	81
NaHCO₃ titer	25
NaCl titer	0.5
Per cent decomposition	76
Bottom pressure	6 lb. gauge
Top temperature	85° C.
Top pressure	0.6 lb. gauge

The Manufacture of Caustic Soda. In the manufacture of caustic soda, the decomposition is carried as far as practicable (usually 85-88 per cent) to minimize the waste of lime for causticization.

$$2NaHCO_3 + Ca(OH)_2 \rightarrow CaCO_3 + Na_2CO_3 + 2H_2O$$
$$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2NaOH$$
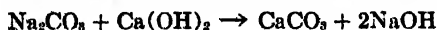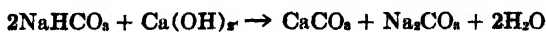
Also, the slurry is made up in such a concentration that the decomposed liquor is of just the right strength for causticization with milk of lime containing about 250 g of CaO per l. In present practice, such a liquor contains an equivalent of 18 per cent Na_2CO_3 as it is delivered to the causticizing tanks. For such purpose, the slurry is made up with the "return liquors" containing about 400 kg. ammonia soda per 1000 kg. of return liquors. As the salt will be accumulated in the decomposed liquor by using the return liquors over and over again, a portion is constantly bled out and sent to the ammonia distiller. The decomposed liquor is kept in the hot condition in a storage properly insulated against heat loss, and sent to the causticizers or reaction agitators, into which a calculated quantity of milk of lime is continuously added for causticization. Details of the operation are given in Chapter XIX to which the reader is referred. This operation avoids calcination of the sodium bicarbonate to soda ash, and then dissolves the ash to make the liquor for causticization. Also, the heat in the liquor from the decomposer is directly utilized in causticization. As far as the CO_2 recovery is concerned, it can be more readily obtained in a rich form by wet calcination than by dry calcination, such as in the rotary dryers, where rotating parts are difficult to make perfectly air-tight. The following represent a typical condition of operation:

TABLE 132. Composition of Slurry for Caustic Soda Manufacture.

Slurry contains	400 kg. bicarbonate on dry basis per 1000 kg. return liquor
Total titer	90
Na_2CO_3 titer	77
$NaHCO_3$ titer	13
NaCl titer	0.3
Per cent decomposition	86
Bottom pressure	6 lb. gauge
Top temperature	85
Top pressure	0.6 lb. gauge

As we are concerned here with a high degree of decomposition, we must make our best effort to reduce the bicarbonate in the liquor as far as possible. It will be noticed that the slurry used here contains less bicarbonate. One reason why we do not use a more concentrated slurry here is that a much higher concentration of the slurry would lead to a region where sesquicarbonate would be formed, from which CO_2 is liberated only with difficulty. (See Fig. 99.) Then again in caustic soda manufacture, we do not need a more concentrated decomposed liquor for causticization.

For each of the foregoing three processes, to which wet calcination is applied, a diagram may be drawn to represent each condition. In the diagram (Fig. 99) the ordinate is the number of mols of H_2O per mol of Na, while the abscissa is the degree of decomposition. The degree of decomposition in sodium bicarbonate is represented by zero, while that in soda ash is represented by 100 per cent. Axis-OY represents the composition of the slurry in mols of H_2O per mol of Na, while Axis-OX repre-
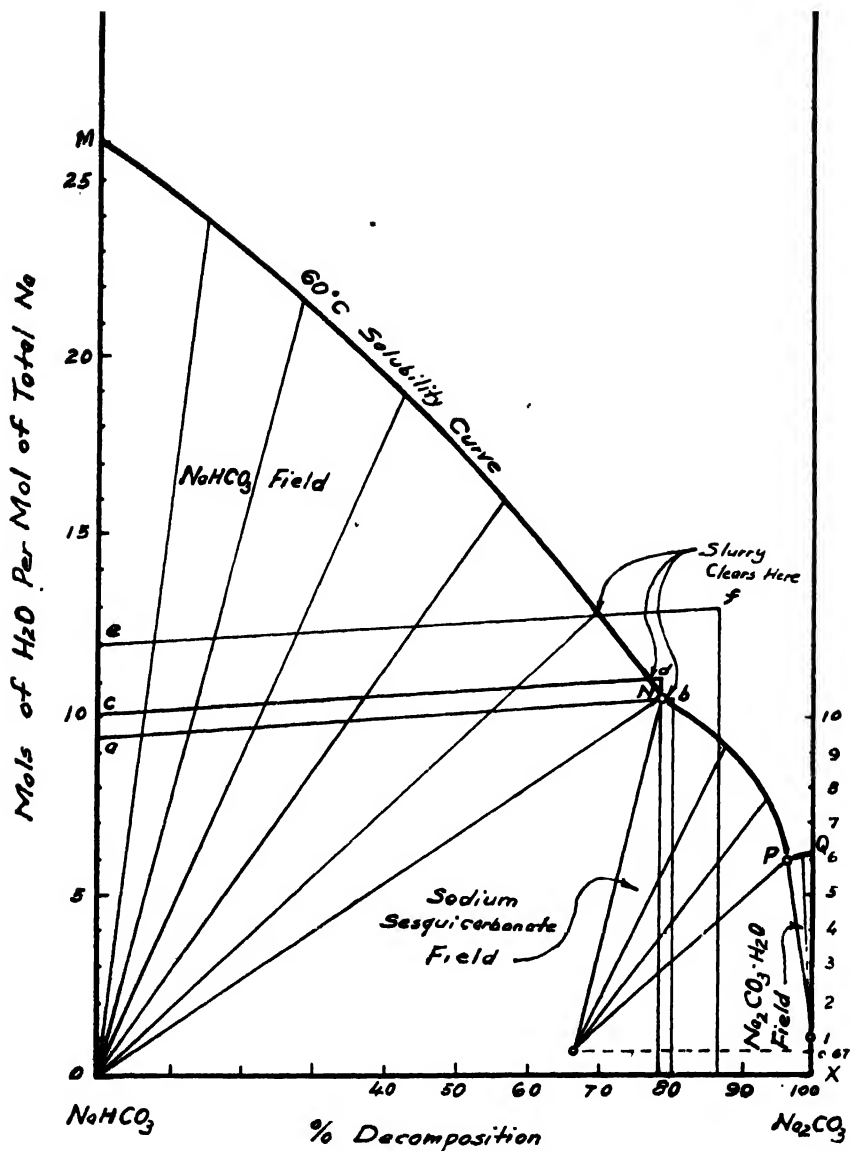
FIG. 99. Process diagram for wet calcination.

sents progress of decomposition. Lines ab, cd, ef represent wet calcination for the manufacture of sodium sesquicarbonate, refined sodium bicarbonate and caustic soda, respectively. The end of the line b, d, or f represents percent decomposition at the outlet from the decomposer. The inclination of these lines upward indicates dilution of the liquor during decomposition, due to steam condensate in the decomposer and water

formed from the decomposition. The curves MN, NP and PQ are solubility curves for pure sodium bicarbonate, sodium sesquicarbonate, and sodium carbonate monohydrate around 60° C. respectively.

The heat required for wet calcination in caustic soda manufacture may be estimated as follows:

Given:

Slurry contains per 1000 kg. water,	400 kg. $NaHCO_3$ on dry basis
Sp. gr. of slurry	1.21
Sp. heat	0.84
Temperature of slurry feed	40° C.
Exhaust steam	6 lbs. gauge
Temperature at top of decomposer	85° C.
Pressure at top of decomposer	0.6 lb/□″ gauge
Steam pressure at 85° C.	8.4 lb/□″ abs.
Bicarbonate required on dry basis per 1000 kg. soda ash	1580 kg.
Slurry required per 1000 kg. of soda ash $1400 \times \dfrac{1580}{400}$	5500 kg.

∴ Heat Required for Wet Calcination:

1. Heat of solution of 1580 kg. $NaHCO_3$ at 4300 kg. cal per mol

$$1580 \times \frac{4300}{84} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad 80,900 \text{ kg. Cal.}$$

2. Heat required to heat bicarbonate solution from 40 to 100° C.

$$5500 \times 0.84 \times (100-40) \quad \dots\dots\dots\dots \quad 277,000 \text{ kg. Cal.}$$

3. Heat required to drive out CO_2 gas from solution

$$\frac{1580}{84} \times \frac{1}{2} \times 86\% \times 5880 \quad \dots\dots\dots\dots\dots \quad 47,600 \text{ kg. Cal.}$$

4. Heat carried off in steam at 85° C. from decomposer top

$$\frac{1580}{84} \times \frac{1}{2} \times 86\% \times \frac{8.4}{15.3-8.4} \times 18 \times 548 \quad \dots\dots\dots \quad 97,100 \text{ kg. Cal.}$$

$$\text{Net total heat required} \quad \dots\dots\dots\dots\dots\dots \quad 502,600 \text{ kg. Cal.}$$

$$\text{Heat loss through radiation, etc. (say 20\%)} \quad \dots\dots\dots\dots \quad 100,500 \text{ kg. Cal.}$$

$$\text{Total} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad 603,100 \text{ kg. Cal.}$$

Heat to be supplied from low-pressure steam:

Latent heat available in exhaust steam at 6 lb. gauge = 532 kg. Cal.
Wt. of exhaust steam at 6 lbs. gauge

$$= \frac{603,100}{532} = 1130 \text{ kg. steam.}$$

This is a rough estimate. In plant practice, the figure is nearly 1.2 metric ton of steam per metric ton of soda ash. This is considerably less than the quantity of exhaust steam required for ammonia distillation, namely about 2 metric tons of exhaust steam per metric ton of soda ash output.

Chapter XXII

Generation of Power for Ammonia Soda Plants

The requirements in the generation of power for ammonia soda manufacture are not in any way fundamentally different from those in any other chemical industry, except that as the exhaust steam is used for ammonia distillation, the plant generally runs non-condensing or uses bleeder turbines. As the buildings in ammonia soda plants are, as a rule, tall and the machinery is scattered, individual drive by electric motors is undoubtedly the best arrangement. Among the largest units that require steam are the electric alternators, or turbo-generators, which are used for power as well as for lighting, the power required for lighting being about 10 per cent of the total electric power generated, although this figure varies with the layout of the plant. The next largest units requiring steam are the CO_2 compressors. Then come the cooling water pumps, the air compressors, the filter vacuum pumps or "exhausters," the absorber "exhausters," etc., all of which may be steam-driven to produce exhaust steam enough for ammonia distillation and to secure flexibility in speed regulation to meet the different demands of changing conditions.

For low-speed drive, the horizontal, duplex, steam-driven type is best suited and should be recommended for the construction of all these machines. In certain cases, however, the single-cylinder, horizontal type may be used to advantage, as in the case of the CO_2 compressors, since each compressor can be better regulated to suit the individual column-operating conditions. The vertical type is not recommended as it does not possess high stability, nor can it withstand heavy duty. Corliss valves in different forms are commonly used. Standard Corliss valves are recommended for low speeds, non-releasing Corliss valves for higher speeds, and half Corliss for the inlet valves of CO_2 and air cylinders. Recently "Unaflow" steam engines have been extensively used, and have given better economy than countercurrent type engines. Exhaust steam is piped in 16- to 24-inch mains to the distillers. The exhaust from the feed-water pumps for the boilers and other auxiliaries should also be introduced into the exhaust main. As there is normally a scarcity of exhaust steam for ammonia distillation, every bit should be conserved and not allowed to escape into the atmosphere. If, however, the steam valves and piston rings in the engine cylinders leak because they are worn out by use, there would be an excessive quantity of exhaust steam. Under these conditions, there would be a tremendous demand for steam at the boilers and an excessive amount of coal would be consumed. Leakages of this kind are very serious in Corliss valve cylinders, because steam would leak around the admission valves and pass out directly to the

exhaust main around the exhaust valves at the same end, regardless of
the events in the piston operation. The back pressure then becomes exces-
sive and the engines consume abnormal quantities of steam in order to
develop the required horsepower. A back-pressure valve should, there-
fore, always be provided in the exhaust steam system for atmospheric
relief in case the pressure should go up to an undesirable figure. Further,
as mentioned in Chapter XIV, the volume of the filter liquor for ammonia
distillation should be kept as small as possible so as to require the mini-
mum amount of steam for distillation.

The equipment used outside of the boiler and engine rooms, such as
the centrifugal type of pumps used for brine and strong liquors; the
plunger type of pumps used for mud and milk of lime; stirrers for milk
of lime, for prelimers, and for settling vats; conveyors and elevators of
all kinds—in fact all machinery outside of the power plant—should be
individually electrically driven. They are operated at more or less con-
stant speeds, so that the cheap and rugged squirrel-cage type of motor
is best adapted for the work. This type of motor, of course, calls for A.C.
power which is preferable to D.C. The best voltages considering all
phases would be 440 volts for power and 110 volts for lighting, unless the
motor units are very large, in which case higher voltage, say 2200 volts,
may be used. For all classes of work, except in driving direct-connected
centrifugal pumps, higher synchronous speeds than 1200 r.p.m. are unde-
sirable because of the smaller starting torque in these high-speed motors
and of the expensive speed reduction mechanism necessary. Synchro-
nous speeds of 720, 900 and 1200 r.p.m. are most generally used. All
motors from 50 hp. up should be started with compensators, although this
is largely a matter of electric power plant capacity. Small motors may
be started with across-the-line, full-voltage, magnetic starters with no-
voltage release and overload protection, but motors smaller than 2 or 3
hp. are seldom desirable in plant operation.

In America the preferred electrical characteristics are three-phase,
60-cycle, 440 volts, 550 volts, or any other multiple of 110 volts, while in
Europe three-phase, 50-cycle, and 380/220 volt star-delta connections are
common. The generator and distribution voltage depends on the distance
of the power plant from centers of load. In American alkali practice,
2300 volts is reasonably well standardized. In oil refineries, for example,
where loads are less concentrated, higher voltages such as 6600 volts or
higher, are prevalent. The electric power distribution system of an alkali
plant has a peculiarity in that interruptions to service must be so nearly
non-existent that the service shall be absolutely continuous. It is there-
fore important that service should be given to each building through at
least two different feeders. A common system is to have a feeder for each
building or load center, and in addition, a common circuit or spare feeder
which can feed any one of several load groups. Due to the corrosive
nature of the atmosphere around any chemical plant, electrical distribu-
tion equipment is subjected to rather severe service. It is therefore cus-
tomary to protect feeders, sub-station switch gear, switchboard apparatus,

motor starting equipment, etc. with dust and fume tight enclosures. Standard, open squirrel-cage motors are commonly adopted, although drip-proof motors in certain wet places are desirable; but no explosion-proof type of electrical installation is required. Slip-ring motors are seldom used except in special cases where a high starting duty or regulation of speeds is desirable. Synchronous motors in units above 250 hp. may be installed to advantage for power factor correction, especially in cases where a low speed drive is required. Electric cables are best kept in iron conduits with vapor-tight fittings. The most satisfactory main distribution is to use lead-covered or waterproof, rubber-sheathed cables with power ducts underground which make the plant substantially immune to lightning.

The coal consumption in a soda plant varies greatly with the size of the plant (the output), the efficiency of operation, the equipment in the engine and boiler rooms, and the maintenance and supervision of the equipment. It varies from 0.2 ton of coal per ton of soda ash made in large, well-operated plants to as much as one ton of coal per ton of soda ash made in very small plants.

The question arises as to whether the exhaust steam will be just sufficient to meet the distillation demand, whether live steam will have to be employed in part to meet the distillation demand, or whether too much exhaust steam will be left on hand so that a good portion of it has to be allowed to escape into the atmosphere. To answer this question, many phases have to be considered which concern the economy of the whole plant operation. Any one of the three cases may exist.

Normally there is a tendency toward a deficiency of exhaust steam. It is largely a matter of heat conservation (by means of preheating arrangements for heat regeneration) and the balancing of operations between the engine room and the distillation plant. If the CO_2 gases are dilute, considerable power is consumed by the CO_2 compressors per ton of soda output, and consequently there is a corresponding increase in the exhaust steam produced from the compressors. If the engine valves and piston rings leak because of poor upkeep of the engines, there is a corresponding increase in the exhaust steam produced. Thus, there may be a large surplus of exhaust steam on hand under these conditions.

If, on the other hand, there is an excessive dilution in the filter liquor and the milk of lime employed is weak, a large amount of exhaust steam is needed for distillation. If the milk of lime is cold and the filter liquor has not been properly preheated before entering the heater, steam consumption in the distillers is greater. Thus there will be a deficiency of exhaust steam to meet the distiller demands under these conditions.

A large volume of filter liquor and other weak liquors to be distilled causes a high static pressure at the bottom of the still and consequently throws a high back pressure on the exhaust main, causing excessive back pressure and high steam consumption in the various engines and bleeder turbines. This creates a greater demand for high-pressure steam from the boilers.

For good economy of plant operation, therefore:

(1) The lime kilns must produce high-test CO_2 gas, and the furnace (dryer) gas must be kept concentrated by guarding against leakage of air into the dryers and the furnace gas system.

(2) The column (tower) decomposition must be kept high so that a smaller volume of mother liquor is produced per ton of soda ash made.

(3) Good bicarbonate crystals must be maintained in the columns so that a smaller amount of wash water is required on the filters to keep the salt content in the ash below a maximum, thereby preventing unnecessary dilution of the filter liquor, and so that the bicarbonate crystals will filter dry, thereby cutting down coal consumption in the soda dryers. The wash water must be accurately maintained at the optimum temperature and properly distributed across the filter surface to effect efficient washing.

(4) The filter liquor must be kept concentrated and no more waste or weak liquors should be sent to it than necessary.

(5) The filter liquor must be preheated in distiller condensers to a high temperature before entering the heater.

(6) The milk of lime must be used hot, and hot water from the exit of the condensers or coolers should be used for making the milk of lime in the slaker.

(7) The milk of lime must have a high concentration of lime so that as little water is introduced into the milk of lime as possible (cf. attempt to use dry lime in prelimers).

(8) All valves and piston rings in the steam cylinders must be kept tight and in good condition, and the setting of these valves must be frequently checked by indicator cards or otherwise. All power equipment, such as the compressor end of CO_2 compressors, steam engines, or turbines driving them, and all mechanical valves, must be kept as efficient as possible (low efficiency revealing itself in hot bearings, high oil consumption or rapid wearing out of these moving parts).

(9) All steam piping, distillers, prelimers, and other hot vessels should be adequately lagged with sufficient thickness of heat-insulating materials, and all the condensate contained in the exhaust steam should be trapped off at the distiller end as well as in the exhaust steam main so that only dry, saturated steam enters the distiller.

(10) Plants must be provided with an adequate number of meters and indicators which will also record the periods and amounts of exhaust steam passing through the reducing valves or blowing to the atmosphere. Frequently, under maladroit control, a plant operating near the balance point has steam going through the reducing valve and at the same time blowing to the atmosphere.

(11) The equipment units, or trains of connected apparatus, should not be too large for the plant. They should be small enough to permit

certain units to be taken entirely out of operation during a slow-down. This, of course, must be done consistently with the requirements for low direct operating labor costs.

(12) Apparatus on the dry side of the plant should be arranged for minimum rehandling of products.

(13) At the boiler end, the boiler feed water made up of the exit hot water from the different condensers and coolers must be preheated to a high temperature in economizers heated by flue gases, and further in heaters heated by exhaust steam, before entering the boilers. Economizers under certain conditions may be installed at the back of the soda ash dryers to recover the heat from the high-temperature flue gases there. Air preheaters and extraction steam feed-water preheaters may be considered if the plant fuel costs warrant them.

All these factors tend to reduce coal consumption for the whole plant, so that, given a good boiler outfit, with the usual necessary accessories for a modern steam-generating plant, a good coal figure per ton of soda ash made will be shown.

Boiler feed water can (more or less successively) receive waste heat from:

(1) Distiller condensers
(2) Furnace gas cooler
(3) Steam flashed from distiller blow-off
(4) Rotary dryer-economizer
(5) Extraction steam
(6) Boiler plant "steaming" economizer

Steam flashed from distiller blow-off is better used in "weak liquor" distillation. This is the distillation of ammonia from weak ammonia-bearing liquors, from the condensate resulting from the cooling of the furnace gases and from the calcium and magnesium sludges settling out of the ammoniated brines. Soda dryer economizers are expensive and, where the feed water is still quite cold, often have high maintenance cost because of corrosive condensate on the flue-gas side during a slow-down. Extraction steam preheating is justified only with fairly expensive fuel. The boiler plant economizer is today built as a "steaming" economizer and as such is most generally justifiable.

A modern steam generating plant minimizes the waste of heat, and recovers the sensible heat from the flue gases as far as possible. The furnace is usually provided with an induced-draft fan and a forced-draft blower, yielding a balanced draft which causes the least possible leakage of air into the furnaces. Air for combustion is preheated by means of the flue gases in the air-preheater, and the feed water on its way to the boiler is first preheated in the economizers heated by the flue gases, and then in the feed-water heater and deaerator heated by the exhaust or extraction steam. Often, the intake air is led through ducts in the furnace walls to cool the fire-bricks and also to preheat the air. Frequently,

water-cooled walls are provided, especially when pulverized coal is fired, and a number of water tubes leading from the steam drums above are located around the combustion chamber to absorb the radiant heat from the rolling flame as well as to protect the fire-bricks from exposure to this intense heat. In this way, a high rating of the boiler is secured. People nowadays seldom figure on the normal rating of one B.H.P. per ten square feet of heating surface. From three to five hundred per cent of this normal rating is often not difficult to obtain.

As mentioned above, the generator turbines should preferably be of the bleeder type with condensing outfits, but having automatic bleeding points to bleed out extraction steam for pressures varying from 8 to 10 lbs. per sq. in. depending upon the requirements for ammonia distillation. To take care of any unbalanced conditions between the amount of exhaust steam required and the amount of exhaust steam at hand, steam may be bled out from this unit in any desired quantities to make up the deficit, while the remainder goes to the condenser. Thus, just sufficient exhaust steam to meet the distiller requirements may be maintained without wastage.

Another good feature is that mixed steam pressures can be used. The present tendency is toward high working pressures. If old, low-pressure boilers and engines are still in use in the plant and it is considered that they are still too good to be scrapped, then mixed steam pressures must be employed. New, high-pressure units will be working together with old, low-pressure units. The high-pressure steam can be employed to advantage in the bleeder type turbo-generators running condensing, and the extraction steam from the bleeder at a lower pressure can be utilized to drive the low-pressure engines or low-pressure turbines, so that the amount of exhaust steam from the low-pressure cylinders can be adjusted to meet the demand of the distillers. Furthermore, if there is, for some reason, a shortage in the high-pressure steam, the low-pressure steam can actually be introduced backwards into the turbo-generator through the bleeder connection to meet the generator load. If the old equipment both at the boiler and engine ends operates at 200 or 180 pounds steam pressure and it is desired to install larger units working at 900 or 600 pounds steam pressure, a high-pressure bleeder type turbo-generator taking steam at 900 or 600 pounds pressure can be installed to advantage, and the extraction steam at 200 or 180 pounds pressure taken out to run the low-pressure engines or turbines.

For the same reasons at the electric end, when many induction motors of comparatively low speeds and small capacities have been installed throughout the plant for a number of years, the power factor of the plant is likely to be low and the power losses high. To correct the power factor in such a plant, several synchronous motors in large units may be purchased when certain large units of constant-speed machinery are to be installed, or else a capacitator of sufficient size may be installed on the main feeders.

A still more flexible arrangement is to make an agreement with the

city or local power company, whereby electric current from the city line can be drawn to meet a part of the demand in the plant whenever a surplus of exhaust steam is being accumulated, *i.e.*, during periods of low production. The current will be returned to the city line when the plant is in full operation producing all the exhaust steam required, *i.e.*, during the time when large quantities of exhaust steam are required for distillation because of the increased output.

During recent decades, the rapid improvement in high-pressure and high-temperature steam- and power-generating equipment has permitted the ammonia soda industry to produce a large number of surplus kilowatt hours without increased (and at times with decreased) coal consumption. Practically every American plant has taken advantage of this development in connection with the installation of adjacent electrolytic caustic operations. Only three of the ten plants operating in the United States are, as of 1939, without electrolytic caustic operations. As late as 1926 a steam pressure of 150-200 pounds gauge and a temperature of 500° F. was among the highest in the industry, and was representative of fairly uniform practice in America. Steam conditions in certain alkali plants in 1939 have reached as high as 2500 lbs. per sq. in. and 950° F., but 450-, 600- and 900-pound pressure plants are in general operation.

The power requirements of an ammonia soda plant revolve around the two major consumptions which are, (1) low-pressure steam for ammonia distillation, and (2) power for compressing gases and elevating the brines. The first figure is generally of the order of 4000 pounds of steam per ton of soda, and the second is of the order of 75 kilowatt hours per ton of soda. As stated throughout this volume, figures of this character vary widely from plant to plant. Variations in the above correspond to the variations in coal consumption given in Table 148. In some cases high coal consumption may be due to the profit resulting from burning a local, but inferior grade of coal, or from some other condition not indicative of low efficiency. Other requirements for steam and power are space heating in the winter time, the various pumps, the operation of all agitators, conveyors, elevators, rotary calciners, filters, power plant auxiliaries, etc., as stated above.

All mechanical power requirements in an ammonia soda plant can be

TABLE 133. Types of Drive for Machinery in Alkali Plant.

Load	Driver
Electric generators	Steam turbines, bleeder or straight condensing
Carbonating tower gas compressors	Horizontal reciprocating steam engines, or steam turbine in centrifugal compressors
Pumps for main supply of cooling water	Steam turbines or electric motors
Pumps for handling brine and intermediate liquors	Electric motors
Elevators, conveyors, agitators, etc.	Electric motors
Filter vacuum pumps and absorber vacuum pumps	Steam engines, steam turbines or electric motors

arranged for electric motors, reciprocating steam engines, steam turbines and even water turbines or internal combustion drives. In present practice, those given in Table 133 are usual.

Because of the convenience of wiring in the tall buildings and scattered machinery necessary for the most economical arrangement in the process, all drives smaller than about 75 or 100 horsepower are usually electric motors. The combined efficiency of a large turbo-generator, electric transmission wire and induction motor is superior to any other under such conditions. From the maintenance cost standpoint such combination is also decidedly superior.

As one requirement for the ammonia soda power plant is to run the plant non-condensing or with bleeder turbines with a back pressure of about 10 pounds gauge, any efficiency in the utilization of heat must come from the use of higher steam pressure and superheated steam. For the higher steam pressure and the presence of high superheat mean a higher initial temperature for the working fluid. According to the Second Law of Thermodynamics, the maximum possible efficiency in utilizing the heat (*i.e.*, for a reversible process) is given by the fraction $\dfrac{T_1 - T_2}{T_1}$, where T_1 is the initial absolute temperature and T_2 the final absolute temperature of the working fluid. As we cannot run the engines entirely condensing, little can be done with T_2, and the only thing left to do is to boost T_1, *i.e.*, to employ a higher steam pressure and greater superheat in the steam, in order to make the value of this fraction as large as possible. The modern tendency in soda ash plants, as in the case of central power stations, is to use high working pressure and high superheat.

The heats of formation (from the elements) for the raw materials and final products of the overall chemical process of the ammonia soda industry very nearly cancel each other. Hence consumption of coal in a simple ammonia soda plant, on the basis of the First Law of Thermodynamics, would be almost zero. On the contrary, as seen from the data given on page 516 and in Table 148, coal and coke together head the list of expenses of production. Direct operating cost and at times total payroll are generally smaller than the fuel bill, though not invariably so. The overall net reaction in the ammonia soda process:

$$2NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2 \pm \text{small heat effect}$$
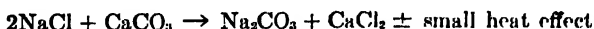
can be compared to the overall performance of an ice-manufacturing operation, the equation for which might, for purposes of this analogy, be stated:

$$\text{Warm water} + \text{cold brine} = \text{warm brine} + \text{ice} \pm \text{``0'' Calories}$$

Therefore, the heat efficiency of an ammonia soda operation must be scrutinized on the basis of the Second Law of Thermodynamics. Its overall operation is analogous to that of any operation whose ideal is the Carnot cycle.

We may write the equation connecting heat and work in the Second Law of Thermodynamics as

$$\frac{dW}{dQ} = \frac{T - T''}{T} = 1 - \frac{T''}{T},$$

wherein dQ represents the differential amount of heat to be extracted from any source of heat (steam, coke fire in kilns, fuel in rotary calciners) at the necessary temperature T, and dW represents the reversible work that can be obtained from this heat on transferring it down to the practical cold reservoir temperature T'' of the plant in question.

If state 1 is taken as the initial condition and state 2 as the final condition of equilibrium at cold reservoir temperature T'', then the above equation integrates to

$$W_1 - W_2 = Q_1 - Q_2' + T'' (S_1 - S_2)$$
$$\left(S = \text{entropy or} \int \frac{dQ}{T} \right)$$

Alkali plants should be compared by the above equation when studying possible heat or fuel improvements. In usual good practice, alkali plants have a Second-law efficiency in the order of 40 to 50 per cent. That is, when operating near the most profitable condition for the local costs of fuel and fixed charges for equipment, "good" plants are burning about twice the amount of fuel that is theoretically required. With present technical knowledge and available materials of construction, this efficiency could be increased, but in all probability not much beyond 60 per cent. Still higher efficiency would require untried and uneconomically expensive procedures, such as binary fluid systems, or the decomposition of limestone, the generation of steam power, and the calcination of bicarbonate in series from a single fire, etc.

As to the boilers, nothing but the water-tube type should be considered. The use of a shell type or a fire-tube type in the form of a horizontal return tubular boiler is entirely out of date. Water-tube boilers have many advantages. Chief among them are:

(a) Large grate area (for use with poorer grade coal), large heating surface per rated b.hp., and large steam-generating capacity.

(b) Greater safety and higher mechanical strength in the construction; accidents, if any, occurring in the form of tube fissure rather than shell explosion.

(c) Better circulation of water in the boiler, equalized temperature and uniform expansion in all parts of the boiler, and consequently greater freedom from strains due to unequal expansions.

(d) Quick steaming.

(e) Accessibility for repairs and good facility for cleaning; all scale formed inside the tubes being easy to get at and may be cleaned by means of turbine cleaners.

(f) Higher efficiency and economy in heat utilization.

From the above, it will be seen that a water-tube boiler is suitable from every point of view. In large units a three-drum bent-tube type, or Stirling type, of water-tube boiler is especially well adapted. Although it appears simple to clean the tubes of a straight-tube water-tube boiler, there is likely to be leakage at the rolled joints; whereas in a bent-tube boiler, the tubes are bent so as to take care of their own natural expansion. Therefore, in a bent-tube boiler, tube trouble seldom occurs and removal is rarely necessary. In a straight-tube boiler, especially when it is subject to frequent shut-downs for cleaning, etc., the straight tubes may be bent or twisted to such an extent that the tube ends shrink into the tube sheet at either end. This will necessitate frequent renewal of the boiler tubes.

There are two general types of water-tube boilers available: those where the tubes enter common drums and those where the tubes are brought into relatively small headers. The sharp distinction between these two types has disappeared to some extent in recent years because of the rapidly spreading use of various kinds of "water-wall" furnaces. The latent heat of evaporation of water decreases rapidly with increasing pressure in the water-steam system. Hence, at higher pressures the amount of heat which must be transferred through boiler heating surface for the actual conversion of water into steam is appreciably smaller than at lower pressures. At the same time, the amount of heat which must be transferred through boiler and economizer surface to bring the temperature of the water up to the boiling point is relatively greater. Likewise, at higher pressures the correspondingly high steam temperature requires extended superheater surface. Therefore modern, high-pressure Stirling boilers with water-cooled furnaces often have more tubes entering manifolds than drums. Those parts of a boiler in which the water is below the boiling point are generally referred to now as "economizer sections." These parts may be either actual economizers (operated above boiler pressure) or they may be "steaming" economizers. In the latter case, they are really a part of the "convection" surface of the boiler. In either case, being constructed of a multiplicity of tubes, they should be such that external and internal surfaces are readily accessible for cleaning. The external surfaces, that is, those presented to the fire or products of combustion, should be provided with properly located soot blowers or automatic cleaning devices. The water treatment should be selected so that internal cleaning is very seldom required. This suggestion is made more from the standpoint of operating safety than from that of the reduction of maintenance costs.

In modern boiler equipment there should be a minimum of refractory surface. The highest rates of heat transfer are obtained where absorption of radiant heat is possible. Consequently the "all water-cooled furnace" permits very large steam generating capacities per unit of floor space which, of course, provides a saving in initial cost; and the alkali plant, because of its high fuel consumption, should take advantage of such developments.

The size of the boiler units is best kept relatively small from the standpoint of the shut-downs required for routine inspections. On the other hand, units that are too small unduly increase the initial investment and result in larger direct operating labor cost and in low efficiency.

For a soda plant which requires 1000 b.hp. or more, the boilers should be stoker-fired rather than hand-fired, not only because of limitations of human physical strength, but also because uniformity of operation and economy in utilizing the heat in the coal consumed. If the calorific value of the coal is very low because of high content of ash or foreign matter, special effort should be made to secure extra-large grate area. If the coal has only ten thousand or less B.t.u. per pound, 1 square foot of grate area to 4 to 5 rated b.hp. is none too much. A draft gauge should be provided in every furnace to determine the amount of draft the furnace is carrying. If a CO_2 recorder is not provided, the flue gases should be frequently tested with an Orsat apparatus. The draft that gives the highest CO_2 test in the flue gases should be considered as the optimum for the furnace, and the damper position adjusted accordingly. For large soda plants, especially where larger units of boilers are required and low-grade coal is to be used, pulverized coal with a unit pulverizer system and a high-pressure boiler with water-cooled walls give very good efficiency and economy in the utilization of coal. Pulverized coal does away with stoker firing and simplifies the ash-handling problem materially.

Since fuel is generally, if not always, the largest single item among the operating expenses in alkali plants, it is worth while to consider every possible "heat-trap." Justification of each heat recuperation or the extent thereof depends on the local cost of fuel. If the fuel is coal, as it is in a great majority of alkali plants, a decision must be made as to the method of firing. That is, whether hand firing, automatic stoker or pulverized-coal firing is the most profitable. There is still an open question whether pulverized fuel firing or mechanical stoker firing gives better results all around. In America, pulverized fuel has come to the fore, especially for very large steam-generating units. For steam generating capacity below 35,000 lbs. per hour, however, stoker firing is, as a rule, recommended. In Europe, the stokers still find great favor. With mechanical stokers, the operation is simpler and the first cost is slightly less. Mechanical stokers in Europe have been developed to such a perfection that it is claimed that as good efficiency can be obtained with stokers as with the pulverized coal method, particularly in small units. On the other hand, pulverized fuel firing is adaptable to almost any grade of coal and yields good efficiency in the case of high-ash, low-grade coal, although the power consumed in pulverizing high-ash coal is considerable. The maintenance charge is higher with the pulverized coal system. In localities where the air is humid and there is much rain, the amount of moisture in the coal generally causes trouble in pulverizing, and necessitates a separate coal drying plant when it much exceeds 8-10 per cent.

Chemical treatment or conditioning of the feed water is carried on somewhere in the preheating cycle and its various methods are discussed

in detail in Chapter XXIII. In plants making no caustic, substantially none of the condensate from the steam generated is available for boiler feed water. In plants where the steam requirement of the concentration of caustic is a considerable fraction of the total steam, most of that fraction is available for boiler feed water in the form of the condensate, but it is frequently more desirable to use it for mud washing, etc. Boiler feed water treatment is therefore an important item of expense in connection with the operation of steam plants for soda plant operation. Not only is the water treatment equipment very large per unit of boiler capacity, but the condensates, drips or such other sources of relatively pure water from the processes which are occasionally used, may be contaminated with alkali. This introduces danger of boiler embrittlement. Until the physical chemistry of the cause and prevention of embrittlement is better understood and methods for its control made more precise, the sulfate-to-carbonate ratios recommended by the ASME are probably the safest procedure for the alkali plant operator, except where the drums are fusion-welded.

If the feed water contains considerable temporary hardness and calcium sulfate, an open-type heater operating on the exhaust steam should be used in order to precipitate most of the calcium acid-carbonate and sulfate from the water before it enters the boiler. Where exhaust steam from cylinders is used for boiler feed, the oil must be carefully separated out in an efficient oil separator. Formerly a closed-type heater was used, operating on the exhaust steam. The latter type is now seldom used because leakages are likely to occur at the tube joints and the cleaning of the tubes is rather difficult. Open-type heaters are now made with efficient oil separators and the manufacturers will guarantee complete removal of the oil. Many heaters are now made in the form of deaerating heaters.

The entire operation of a soda plant depends for its economy on the maintenance of continuity, with uniformly maintained accurate control. Hence boilers produce steam at a much more constant rate than in daylight operating industries or in public utilities. There are no daily or diurnal peak-load periods. Likewise there are no noon-hour "valleys" or or other slack spells during which some routine periodic operations like blow-down, soot blowing, fire slicing, etc., can be done better than at another time. For this reason a number of special features are valuable to the boilers and auxiliaries, such as special distribution of soot-blower elements, continuous blow-down equipment and control, several emergency sources of fuel, design for moderate ratings, etc.

Since there is very little difference in seasonal load on an alkali power plant, the equipment is designed to be operated over long periods for greatest economy. The equipment is also designed for a very high "availability factor."

The boiler plant itself, since it is the place where the most costly of a single item of material is consumed, should, in a well operated alkali plant, be kept up-to-date and in first-class operating condition. The

local manager of an alkali plant is most frequently a graduate from the ranks of operators of the chemical equipment. It is, therefore, not unusual to find the power plant a somewhat neglected area insofar as application of the latest improvements is concerned. The boiler house is more often considered a regrettable spot in connection with the operation of an alkali plant than a place where ingenious and careful operation could effect large-scale economies.

On the other hand, all the large pieces of equipment in an alkali boiler plant are the ones usually found in other industries. The boiler plant thus receives a degree of attention thrust upon it from outside sources, which is not accorded to other parts of the plant. That is, sellers of modern improvement devices for power plant equipment, in continually trying to familiarize their potential customers with the advantages to be gained in utilizing such developments, appear frequently at the plant. Unfortunately, many of these bring about a profit to the user in only a portion of the possible cases where they can be applied. Consequently, the alkali power plant operator and the purchasing agent have adopted an attitude of wilful reluctance which occasionally shuts out a useful improvement.

The boilers themselves, as pointed out above, differ from other power plant boilers in that they must be designed for long-period, uniform-load, continuous operation. The happenings which prevent unlimited continuous operation can be divided into two categories:

First, the accumulation of insolubles precipitating from water being evaporated inside the boiler.

Secondly, the accumulation of solid products from the fuel outside.

The boilers must, of course, be primarily designed and operated with due consideration for the particular feed water which is available and its suitable treatment, as will be discussed in Chapter XXIII. They will then come as close as is profitable to being always in condition to have the accumulations of solids removed as solutions or suspensions by blow-down procedures. Such operation will require a boiler to be opened only for quick statutory and insurance inspection, insofar as internal surfaces are concerned.

On the fire side, the accumulations are either ash or soot. Adequate design requires soot blower location to be such that the regular operation thereof leaves no accumulations to be removed during outage. Ash removal must likewise proceed without interference with routine combustion of fuel. Whereas in a normal industrial power plant, clinker masses can perhaps be sliced up by hand during the night shifts, such procedure will surely penalize the night shift's output in an alkali plant.

The steam required for the distillation of ammonia could theoretically be used at highest pressures, but a high-pressure distiller for materials having the properties of ammonia liquors would be an expensive and, more particularly, an unwieldy unit. Furthermore, at the high temperature involved in a pressure still, it is likely that difficult scale-forming

conditions would be set up in that portion of the apparatus which handles the limed solutions. Again, a distiller can be designed which, theoretically at least, can operate at a very low steam pressure in the bottom. Such a still would require mechanical design features to permit low pressure drop throughout the distiller-absorber system. Consequently, its capacity per unit of cross-sectional area would be low. Some operating experience with low-pressure ammonia distillation indicates that scale deposition even more difficult than the present would have to be solved by expensive trial and error methods.
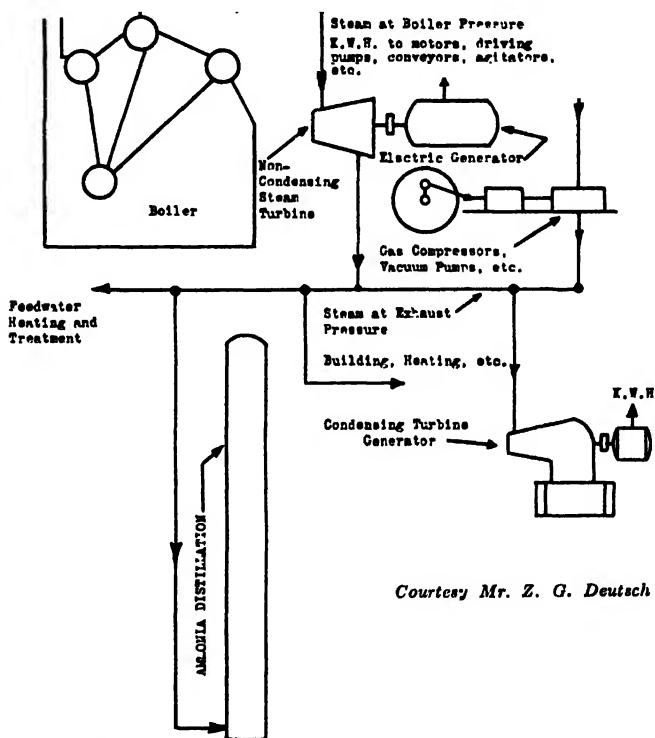
Fig. 100. Diagrammatic connection of power equipment in simple ammonia soda plant.

It is, therefore, universal practice to operate distillers at moderate steam pressures in the bottom, that is, from about 2 pounds below, to a maximum of 10 or 12 pounds above the atmospheric pressure. Since the consumption of steam is large compared to any other unit in the plant (that is, any plant not including chemical caustic or electrolytic caustic operations), it controls the balance of the power plant situation. The prime-movers are collectively arranged to exhaust the required distillation steam, either entirely from electric generators (in a 100 per cent motor-driven plant) or from these and the other steam-driven prime-movers.

In the average (without electrolytic) case, this involves a boiler plant in which steam at a medium pressure and temperature is generated, a portion being delivered to electric generators and the rest to gas compressors, vacuum pumps and turbine-driven water pumps. These all exhaust into a common exhaust main which conducts the steam for the distillation operation and building heating operations. A part of the exhaust steam is also frequently used for the final preheating of the boiler feed water on its way to economizers, located in power plant chimney ducts.
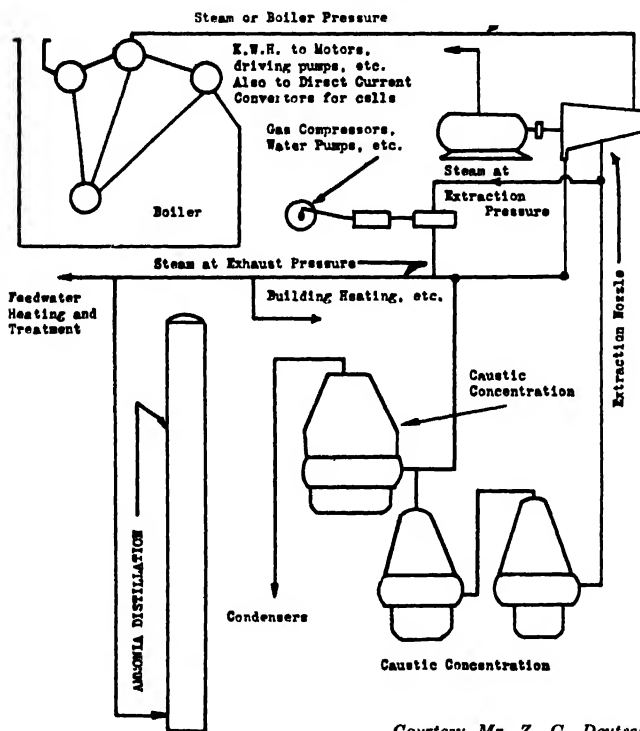
Courtesy Mr. Z. G. Deutsch

FIG. 101. Diagrammatic connection of power equipment in an ammonia soda plant making caustic soda also.

From the foregoing it will be apparent that all mechanical drives, even including the largest, can be electric-motor driven. Then steam at boiler pressure is fed only to the electric generator turbines which exhaust directly to the distillers, etc. This would make a very clean arrangement, but as far as is known it has never proved economical. Fig. 100 shows a diagrammatic connection of power generating and consuming equipment in a simple ammonia soda plant. Fig. 101 shows the same arrangement as applied to an ammonia soda plant which also has chemical caustic soda and electrolytic caustic soda operations served by the same power plant and under the same administration. This latter illustrates the most frequent American practice.

The pressure required at the boiler plant for any one combination of ammonia soda, chemical caustic and electrolytic caustic (and other by-products) can be determined, and curves similar to Fig. 102 can be drawn. These curves are shown with boiler pressure as ordinate, independent of steam temperature. Steam temperature is definitely limited by "creep" of metals and does not influence the total price of boiler equipment up to 750° F., and then causes an increase of price in one step anywhere up to 950° F. (the maximum temperature available today). Therefore, in this elementary discussion it has been eliminated from consideration.
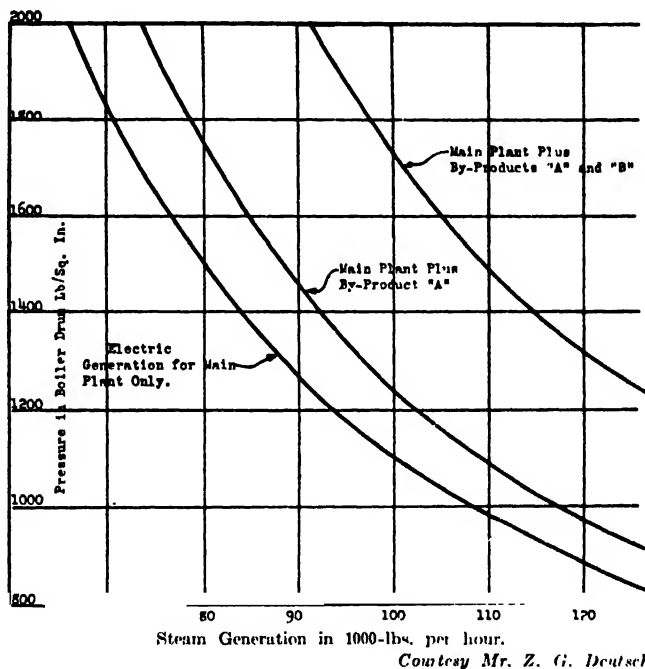
Fig. 102. Relationship between electric power generation and daily output for 900- and 1200-lb. steam pressures. (By-product "A" such as Chemical Caustic and By-product "B" such as Electrolytic Caustic.)

The choice of boiler pressure is then determined by a balance between the increasing cost of boiler plant with increasing boiler pressure and the decreasing cost of fuel resulting from the corresponding lower total steam consumption.

A second and even more important study must be made to determine the best boiler pressure. This has to do with the fluctuation in the rate of production of the various products. That fluctuation is generally not in the control of the plant operating personnel. Best results under circumstances of fluctuating production rates require a different boiler pressure from that for an absolutely steady production.

Fig. 103 shows a Cartesian coördinate, wherein the number of kilowatts

is the ordinate. The abscissa is a non-rigorous function of the plant oper-
ating rate. In a simple ammonia soda plant this can be rigorous, *i.e.*, the
number of tons of soda ash produced per unit of time. In a plant making
both soda ash and chemical caustic, good coördination can be found
when the number of tons of soda ash and the number of tons of caustic
soda produced are merely added together into a "combined" product.
Reasonable coördination is also obtained when electrolytic caustic is
added to the other products to form a "combined" total for plant pro-
duction. It is immediately apparent that wide variations in the pro-
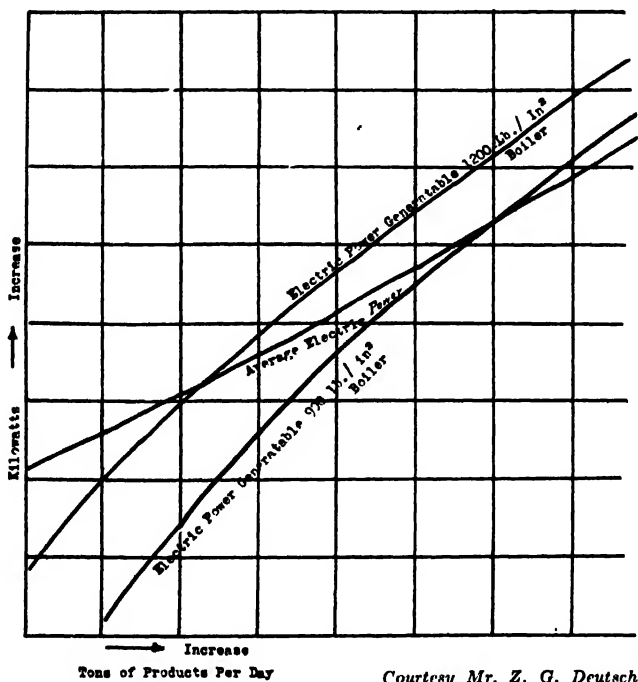
Courtesy Mr. Z. G. Deutsch

FIG. 103. Relationship of steam pressures to output of
products manufactured.

duction rate of one product relative to the others render such a chart
quite inconclusive. However, since the combination of circumstances
which underlie wide fluctuations in the rate of plant production generally
affects all of the products alike, ratios are reasonably well maintained
regardless of the production rate. This type of chart is found to be very
useful in determining the most profitable boiler pressure, either when
designing an entirely new plant, when replacing obsolete power-generating
equipment, or when considering the extension of power generating equip-
ment (topping plant) needed in connection with expansion of production
or addition of new products.

As indicated by the crossed curves on Fig. 103, it is characteristic of

the modern equipment of an ammonia soda plant to have a deficiency of electric energy available at low rates of operation and an excess at high rates of operation. This is because the efficiency of mechanical drives goes down sharply at low loads, whereas the efficiency of steam consumers does not. For example, the electric motor which drives the agitator in the prelimer tank will take exactly as much power, whether that particular distiller assembly is operating at 100 tons per day or at 200 tons per day. Where several distillers and prelimers are being operated in parallel at high rates and one or more are shut down entirely at lower outputs of ash, the electric power drops proportionately; but such control is seldom available. In either case, to a greater or less degree, the steam consumption drops in almost exact proportion to the production, whereas electric power consumption does not. Many of the other electric loads, like screw conveyors, are analogous to the agitator load used for the illustration above. With a large number of the motors (such as drives for bucket conveyors or centrifugal pumps), when the output of the plant is reduced, the load falls somewhat, but not in direct proportion. In Fig. 103, the two curves with the steeper slopes represent the electric power which can be generated by sending the demanded process steam, at either of two boiler pressures, through turbo-generators of average efficiency. The single flatter curve represents the demand for electric power corresponding to the output of products. It is apparent from the chart that a "balance point" exists for each boiler pressure in a given plant. This is the optimum production rate at which there is neither deficiency nor excess of electric energy. It is an invariable practice to bypass steam from boiler pressure through a pressure-reducing valve at production rates higher than the balance point. At production rates lower than the balance point, either the excess exhaust steam from power generation is blown to the atmosphere or the deficiency of electricity is made up in condensing units. This deficiency in electric power may also be purchased from a public utility or adjacent outside concern in the rare cases where such procedure is possible. In large plants where, through the years that they have grown, a variety of types of boiler and electric generating equipment are in operation or available for operation, the plant can usually be kept "in balance" by an interchange of load between high-pressure and low-pressure stations, or between condensing and non-condensing units. Smaller, simple ammonia soda plants get the balance point down to the lowest output not requiring excessively expensive boilers, and then depend on the simplicity of the reducing valve for giving a good year-in, year-out efficiency.

In many of the soda plants, all the large engines and mechanical drives, the gas compressors, water pumps, air compressors, etc., are considered to be within the province of the "generation of power." In the following, a brief discussion of the merits of various forms of such equipment is given. An effort is made to show why local conditions affect choice of the type of equipment.

The gas compressors for compressing lime-kiln, rotary dryer or mixed

gases into carbonating towers (columns) are pieces of equipment most expensive to buy and to maintain in the power end of the ammonia soda business. Regardless of the degree to which lime kiln gases and rotary dryer gases are scrubbed, an amount of dust finds its way into the compressors. The industry has gradually evolved suitable poppet, plate, and rotary types of valves for the gas compressors. These valves are generally of such physical dimensions that slow-speed reciprocating engines are almost mandatory. Low piston speeds from 450 to 500 feet per minute are considered desirable. Recently the introduction of stainless steel, suitably resistant to the corrosive action of the gas, has permitted some progress with "Feather" valves. This requires a special lubricant and lubricating procedure. Inlet valves on the gas end of the compressors are generally of the half Corliss type without the trip-mechanism. Stainless steel piston rods and metallic packings in gas cylinders as well as in steam cylinders have in recent years reduced maintenance costs considerably. Central lubricating systems for steam end and mechanical parts, with dilute soda solution system for gas ends also tend toward lower maintenance cost. The heavy, mechanically operated gas delivery valves require engines of very rigid·frame and bearing design. These mechanically operated valves have done away with much valve trouble. These compressors are generally more expensive per cubic foot of gas compressed on account of low piston speeds than are ordinary air compressors.

Some rotary cycloidal compressors have been used in small capacities; and these units, although quite inexpensive, and of relatively low maintenance cost in larger capacities, are low in efficiency except at some one particular rate of operation or discharge pressure. Recently the industry has shown interest in the centrifugal (or turbo) compressor because of its considerably lower first costs. These units are rarely profitable for a small plant, but show a decided advantage for a very large plant. The approximate dividing point between the "large" and "small" designation depends on a number of factors peculiar to local conditions. In plants using the double entry system at the making columns, the pure lime kiln gas will be profitably compressed into the top entry by centrifugal compressors, in capacities as low as 4000 cubic feet per minute. The bottom entry requires one or two more stages in the centrifugal compressor, but units smaller than 5000 cubic feet per minute would usually favor the reciprocating machines. The centrifugal machines are generally direct-driven by turbines, taking steam at boiler pressure. When they are motor-driven, economy of materials usually dictates a step-up gear set. The centrifugal compressor has a decided advantage in low maintenance and first cost, but generally a decided disadvantage in thermal efficiency. Further disadvantages of the centrifugal compressors are (1) that they are not positive enough in forcing the gas into the columns like the piston-type compressors; (2) that their efficiencies are low, especially in small units; and (3) that their output is so large that several columns have to be served in parallel by one machine, causing difficulty in adjusting the volume of the gas delivered to each column from a common main.

The detailed requirements of the compressor end as to internal design and materials of construction are not yet standardized to the same degree as in reciprocating compressor construction. Another disadvantage, or rather point of objection to the high-capacity centrifugal compressor, particularly where plants are large enough to justify its adoption, is that the single unit requires installation of regulating devices for distributing gas from a common discharge manifold to the several carbonating towers. In the case of the smaller capacity reciprocating machines, one machine, or one cylinder of a duplex machine, or even one end of a cylinder, is separately piped to each carbonating tower. Hence no volume regulation beyond the speed of the compressor is required.

The vacuum pump for pulling air through the filter cake of crude bicarbonate is another piece of mechanical equipment peculiar to the industry. The air is generally scrubbed (on the suction side of these pumps) with cold brine to remove ammonia. The gas contains some CO_2 flashed off from the mother liquor under the action of reduced pressure inside the filter, and also contains a minute amount of brine spray and perhaps also a little mother liquor. The most complete practical separation of these sprays is of great importance to the low maintenance costs of the vacuum engines. Reciprocating vacuum pumps, with valves similar to those described for the gas compressors, are used extensively. The rotary type of positive displacement vacuum pump may be used in relatively small capacity units. The rotary pump of slide vane type, such as made by Fuller Company, Catasauqua, Pa., may also be used. The gas handled by these machines is from 3 to 8 per cent CO_2. The development of superior corrosion-resisting materials of construction has permitted operation of such units with the scrubber on the discharge side. This reduces the vacuum piping cost materially and also reduces the size of both the vacuum pump and the scrubber.

The exhausters for removing non-condensing gas from the ammonia absorber train may be similar to the filter vacuum pumps described above. In the older ammonia soda plants, the absorber vacuum pump was about $\frac{1}{4}$ to $\frac{1}{2}$ the size of the filter vacuum pump. In modern plants, with the efficient types of absorbers made possible by purification of brine, these vacuum pumps become extremely small, since CO_2 is absorbed much more readily by ammoniacal brine in a ceramic-ring packed than in a bubble-cap washer. Consequently, as there is practically no other "non-condensable" gas in the distiller-absorber system except the residual air, the absorber vacuum pump becomes a small control mechanism, rather than a high volume exhauster, provided there is no leakage of air in the vacuum system.

Air compressors for the air requirements of the ammonia soda plant do not differ from those of any other industrial plant. Compressed air is an expensive commodity, often too lightly regarded. There is generally no justification for the use of compressed air for tank agitation, inducing chminey drafts, cooling hot bearings, etc. As an aid to extensive maintenance work, it is almost indispensable, but its indiscriminate use for

other purposes should be carefully guarded against in order to avoid waste of power and consequent high fuel consumption per ton of soda ash made.

The cooling water pumps in ammonia soda plants are generally of a very normal design. The height of the water outlet in the carbonating (making) towers and the distiller condensers generally determines the total head to be carried. Water pumping plant heads of about 130 to 150 feet are therefore normal, provided the pump capacity is adequate. In plants having various pieces of other water-cooled equipment requiring different heads, for example, caustic liquor evaporator condensers, it will often pay to have a two-head system. The materials of construction for the pumps will depend principally on the nature of the impurities in the cooling water supply. In general, a cast-iron pump with bronze fittings is suitable, but for the sake of interchangeability, an all-iron construction is preferable.

Electric generators required for the ammonia soda industry are tailor-made to fit the balance which exists. The turbine generator manufacturers have highly developed designs which can be arranged to be applicable to any condition met in the industry. In general, the equipment should be governed for constant speeds with a voltage regulator and a constant and adjustable extraction steam pressure. Two-pole machines directly driven by extraction-type steam turbines are the modern preference in America. Sizes today range from a minimum of 1000 kw. up to perhaps 10,000 kw. in single units.

As regards feed water pumps for the boilers, it is good practice to have at least two independent units; one unit motor-driven and the other turbine-driven, and in addition one steam ejector for the emergency second reserve. The steam ejector is simple, convenient and economical, and may be connected to a cold water supply for certainty of operation. The ejector will produce a pressure of from 50 to 80 lbs. per sq. in. greater than the boiler pressure and can tide over any period of emergency. But it is not to be used, unless both the motor-driven and the steam-driven pumps are out of commission; which indeed very rarely happens.

Chapter XXIII

Boiler Operation and Conditioning of Boiler Feed and Cooling Water in Ammonia Soda Plants

In an ammonia soda plant, where high steam pressures are used, feed water becomes a matter of increased importance. The problem in an ammonia soda works is aggravated by the fact that, as little returned condensate is available for the boiler feed, almost 100 per cent make-up is required. This situation presents a problem common to many chemical industries where exhaust steam is utilized in the process. Hence in what follows, while attention is confined to the requirements of ammonia soda plants, much of the discussion applies equally well to industrial chemical plants in general.

We shall begin with a general treatment of the subject. Modern steam generators require rather pure water for steam generation, not only because of the high working pressure maintained, but also because of high steam generating rate, particularly when pulverized fuel is used with water-cooled walls. Today, the boiler rating is no longer 10 sq. ft. of heating surface per boiler horsepower (B.H.P.), but generally a figure of from 200 to 400 per cent of this rating. This, of course, calls for a very high rate of heat transmission through the metal walls and requires good, pure water to keep the internal surface clean.

No natural water (not even rain water on account of dissolved oxygen) may be used directly in such boilers without some form of treatment. The nearest approach to a pure water would be distilled water or the condensate from the steam system; but even in these cases the water may not be completely free from oil or dissolved oxygen and CO_2, nor can it be of proper alkalinity (suitable pH) to prevent corrosion in the boilers. All natural waters contain more or less dissolved solids and suspended matter, and the feed water as received in the boiler room may contain, besides these mineral matters, oil, grease, organic matter, dissolved oxygen and CO_2, etc. All these constituents have specific effects on boiler operation.

To summarize, the boiler feed water, if not properly cared for, may contain the following:

(a) Solids: (1) Soluble: mineral matters, alkali salts, alkaline-earth salts, (2) Suspended: sand, clay, organic matter.

(b) Liquids: oil, grease, etc. (mostly from the lubricating medium).

(c) Gases: oxygen (from dissolved air), CO_2 (from alkaline bicarbonates and carbonate hardness).

Raw make-up water comes from two main sources: (1) surface water and (2) artesian well water. Surface water may be lake water, river water, surface stream or any body of water collected from the drain over the earth surface. Such water can be quite "soft," but sometimes also "hard." Mountains stream and falls generally give soft water. Artesian well water comes from underground layers of some depth below the surface (200 feet or more). This is water that flows through underground gravel layers or sand-bearing strata. It is generally a hard water, but sometimes it may contain high alkaline bicarbonates with practically no hardness. The source, therefore, does not disclose the character of the water.

According to the character of the water we may therefore classify water for boiler purposes as follows:

1. Hard: Temporary hardness   3.' Acid
         Permanent hardness   4. Alkaline
2. Soft.

Hard water is water containing dissolved sulfates, carbonates, chlorides, etc. of calcium, magnesium, iron, etc. If these mineral carbonates are in the form of bicarbonates they can be decomposed by heating, and the resulting normal carbonates of calcium, magnesium, iron, etc. precipitated. Hence water containing these bicarbonates is said to possess "temporary hardness" in contradistinction to the sulfates, chlorides, etc. of calcium, magnesium, etc. which cannot be precipitated by heating and are therefore said to constitute "permanent hardness." "Temporary hardness" is undoubtedly due to the solution of the alkaline-earth carbonates by CO_2 dissolved in water, when the water flows through limestone deposits.

Soft water is water that contains little or no alkaline-earth salts. It may, however, contain considerable quantities of alkali salts, such as $NaHCO_3$, Na_2CO_3, NaCl, and Na_2SO_4, which do not form hard scale in the boilers. From the consideration of boiler operation, however, water containing such soluble salts in large quantities is not viewed with favor. No chemical treatment in the ordinary sense can remove these sodium salts. One possible exception is the "De-Mineralizing" process or the hydrogen exchange "zeolite" treatment (see below). Besides, if these soluble salts exist in the form of sodium carbonate or bicarbonate, they may lead to caustic difficulties in the boiler.

Acid water is water containing free acid (H_2SO_4) or acidic salts [$Al_2(SO_4)_3$, $FeSO_4$, $MgCl_2$, $CaCl_2$, and alkaline-earth bicarbonates]. It may have come from the neighborhood of coal mines or peat regions where water has come into contact with sulfur-bearing minerals, such as the pyrites, which through oxidation form sulfuric acid or sulfates of the metals. Such water is generally also very hard. Treatment of lime and soda followed by a zeolite treatment will render it usable for steam generation.

Alkaline water is water containing alkali bicarbonates and carbonates.

Generally such water contains high bicarbonate of soda but hardness is practically absent. It is very similar to an over-treated water having negative hardness, or alkaline hardness, from the soda-lime treatment. The high alkalinity probably owes its origin to the decomposition of feldspars by the dissolved CO_2, yielding kaolin and potassium (or sodium) carbonate which remains dissolved in the water,

$$Al_2O_3 . K_2 \text{ (or } Na_2\text{)}O . 6SiO_2 + H_2CO_3 + H_2O \rightarrow Al_2O_3 . 2SiO_2 . 2H_2O$$
$$+ K_2CO_3 \text{ (or } Na_2CO_3\text{)} + 4SiO_2$$
$$K_2CO_3 \text{ (or } Na_2CO_3\text{)} + H_2CO_3 \rightarrow 2KHCO_3 \text{ (2NaHCO}_3\text{)}$$
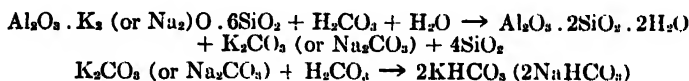
or else to the reaction of calcium and magnesium bicarbonates in contact with natural zeolite bed causing a base exchange, depriving the water of all its hardness,

$$Al_2O_3 . Na_2O . 4SiO_2 . 6H_2O + Ca(HCO_3)_2 \rightarrow Al_2O_3 . CaO . 4SiO_2 . 6H_2O + 2NaHCO_3$$
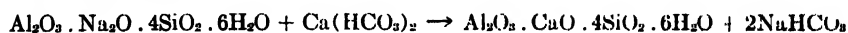
In this way, deep wells sometimes yield water which is not hard, but contains a high concentration of sodium bicarbonate.

Hardness of water is expressed in various ways in different countries. It is, however, generally expressed in terms of $CaCO_3$ except in the German calculation where CaO is used. The following table gives the comparison.

TABLE 134. Comparison of Different Degrees of Hardness.

Parts per Million ppm. or pts/10⁶ or Milligrams per liter (mg/l)	As $CaCO_3$			As CaO
	American Degrees	English Degrees	French Degrees	German Degrees
	Grains per U. S. Gallon (gr.p.g.)	Grams per Imperial Gallon (gr.p.g.)	Parts per 100,000 (pts/10⁵)	Parts per 100,000 (pts/10⁵)
100	$\frac{100}{10^6} \times 7000 \times 8.33 = 5.83$	$\frac{100}{10^6} \times 7000 \times 10 = 7.00$	10.0	$10 \times \frac{56}{100} = 5.60$

Based on ppm. as $CaCO_3$, the American Association of Railway Chemists grading may be expressed as follows, although no strict line can be drawn between different classifications, and opinions may vary considerably with individual water experts.

TABLE 135. Grading of Boiler Feed Water.

Hardness as $CaCO_3$ (ppm.)	Grading
140 or less	Excellent
140 to 260	Good
260 to 350	Fair
350 to 520	Poor
520 to 700	Bad
700 up to 4000	Very bad

Just to show the wide variation in hardness of water from different parts of the country, the following table lists a few of such samples:

TABLE 136. Hardness of Water in Different Localities.

Water Sample	Hardness (ppm.)
Great Lakes water	120
Missouri River water at Omaha, Neb. (April)	215
Chicago Heights City Wells	600
Arkansas River at Little Rock, Ark.	189
Maumee River at Toledo, O.	257
Jacksonville City Wells (Fla.)	274
Red River at Shreveport, La. (January)	86
Greenwood City Wells (Miss.)	35
Detroit River (Detroit, Mich.)	103
Toledo City Wells, O.	1540
Oklahoma Private Wells	4080

Hardness in the boiler water leads to scale formation or incrustation in the tubes and drums. Of the various constituents present in boiler water, the scale formed by calcium sulfate, silica and calcium hydroxide is the hardest and considered serious. The scale is a good insulator of heat and its formation inside the tubes and drums is a matter of grave concern to boiler operators, especially when the boiler is operating at a high rating. On account of excessive local heating of the metal, the tubes may blister or even bulge under pressure, causing damage and serious shutdowns. In bad cases, boiler explosions have occurred causing losses of life and property. In general, as the incrustation is formed, the rate of heat absorption by the metal drops, and the flue gas temperature rises. Following is an estimate of the percentage of heat losses through scale formation in a boiler, as determined at the University of Illinois:

TABLE 137. Heat Losses Caused by Scale Formation.

Thickness of Scale (in.)	Heat Losses (%)		
	(a) Soft Carbonate	(b) Hard Carbonate	(c) Hard Sulfate
1/15	3.5	5.2	3.0
1/32	7.0	8.3	6.0
1/25	8.0	9.9	9.0
1/20	10.0	11.2	11.0
1/16	12.5	12.6	12.6
1/11	16.0	14.3	14.3
1/9	....	16.0	16.0

The above table gives some idea of the magnitude of heat losses, but the figures vary according to the individual boiler setting. Nowadays chemical treatment has reached such a state of perfection that the presence of any scale in the boilers of an ammonia soda plant is no longer considered excusable.

To prevent scale formation in the boilers, chemical treatment is resorted to. The treatment was formerly done inside the boilers (internal treatment) but now more generally outside the boilers (external treatment). Internal treatment was used to a very limited extent in small soda plants which did not warrant investment for a separate water-treating plant and which employed only low pressure steam. In such cases, chemicals such as trisodium or disodium phosphate, sodium aluminate, soda ash, caustic soda, sodium silicate, vegetable tannins or any combination

of these, have been added to the feed water. These are mostly alkaline chemicals and the object is to convert $CaSO_4$, $CaCl_2$, etc. (which form a hard scale) to $Ca_3(PO_4)_2$, $CaCO_3$, etc. which form a loose sludge. Introduction of such strongly alkaline chemicals and organic matter into the boiler, however, is always objectionable and cannot be justified except in very small soda plants with a low working steam pressure (180-160 lbs.). In all cases, the addition of these substances to the feed water increases the soluble solids and alkalinity in the boiler saline, and the phenomena of foaming and priming and even tube ruptures may occur. For steam
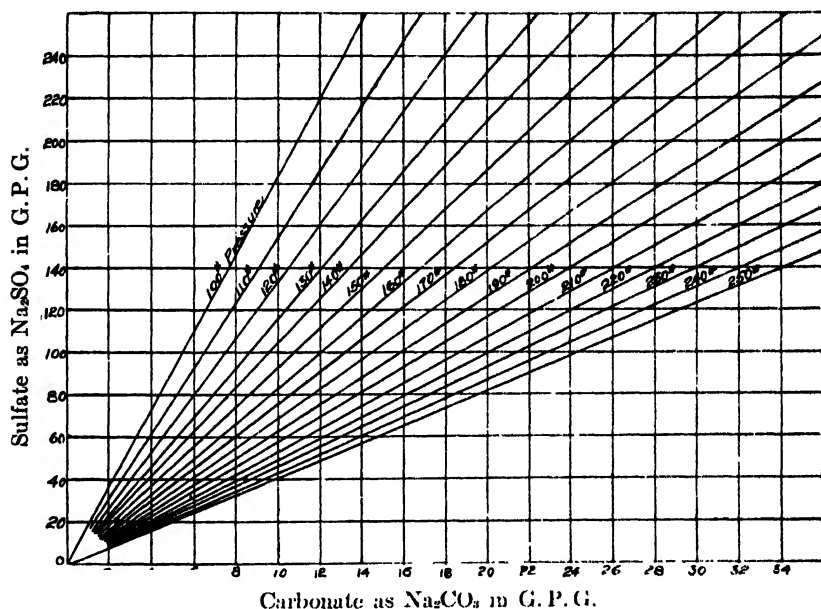
Fig. 104. Curves showing carbonate-to-sulfate ratio in boiler for prevention of hard scale.

pressures above 200 lbs. such internal treatment is not recommended.[*] Fig. 104[†] gives empirical graphs showing the carbonate-to-sulfate ratio that must be maintained to prevent formation of hard scale on the metal walls in the boilers.

These lines show the ratio of carbonate-to-sulfate that must be present in the boiler at a given working pressure to secure loose carbonate scale. Points to the left or above the respective lines mean deficiency in sodium carbonate in the boiler. In using this chart, however, one must always

---

[*] At present, some water experts advocate internal treatment to a limited extent for high-pressure boilers by introducing a portion of raw water into the boilers together with treated water, in conjunction with sludge removal by means of the so-called sludge deconcentrator.

[†] "Boiler Feed and Boiler Water Softening" by H. K. Blauning and A. D. Rich. p. 83, Nickerson and Collins Co., Chicago.

remember that high alkalinity caused by the addition of an excessive amount of soda ash or an alkali in the boiler should be avoided and that safety against caustic embrittlement (see below) should receive first consideration in this treatment.

From the practical side of the boiler operation, difficulties encountered in the boiler room may be one or a combination of the following:

(1) Scale Formation (in tubes and drums) frequently causing bursting of tubes or boiler explosions.

(2) Priming and Foaming (yielding wet steam or causing unsteady water level in the steam drum, or trouble of deposit in the superheater or even on turbine blades).

(3) Corrosion and Pitting (either in the tubes of the economizer, or in the tube heads in the drums or on the drum surface below water level, or at rivet heads of the mud drums).

(4) Caustic Embrittlement (in the plate along riveted joints, or causing bursting of tubes).

A word may be said about the chemical analysis of water and the analytical report on its constituents. Practice varies: some chemists express the constituents in oxide form, such as CaO, MgO, Na_2O, SO_3, etc., while others prefer the ionic form, Ca^{++}, Mg^{++}, Na^+, SO_4^{--}, Cl^-, etc. It is now pretty generally established that the constituents should be expressed in ionic form in p.p.m. (parts per million), or gr.p.g. (grains per gallon), and then in "equivalents per million" (e.p.m.). This last is obtained by dividing grams of each constituent per million grams of water by its combining weight, and is thus equal to milligram equivalents per liter. This has the advantage in that the relationship among various constituents present may be seen at a glance. Take, for example, the composition of a river water, such as water from the Yangtze, the chemical analysis of which, in the winter season, is expressed as follows:

TABLE 138. Chemical Analysis of Yangtze River Water.

Constituents	p.p.m.	Equivalents per million (e.p.m.)
Calcium, as Ca^{++}	41.30	2.065
Magnesium as Mg^{++}	11.44	0.942
Sodium as Na^+	3.86	0.168
Iron oxide and alumina as Fe_2O_3 and Al_2O_3	0.60	....
Bicarbonate as HCO_3	156.5	2.566
Sulfate as SO_4^{--}	22.3	0.465
Chloride as Cl^-	5.10	0.144
Silica as SiO_2	6.4	....
Free CO_2	nil	nil
M.O. alkalinity as $CaCO_3$	130.0	2.60
Total solids	161.2	....
Suspended matter	2.2	....
Organic and volatile matter	22.6	....

If the sum of the e.p.m.'s of Ca and Mg is greater than the e.p.m.'s of HCO_3^-, there is permanent hardness in the water and a hard scale may

be formed in the boilers, if the water is not properly treated. On the other hand, if it is substantially equal to the e.p.m. of HCO_3^-, the water contains only temporary hardness and a soft carbonate scale may be formed. If it is less than the e.p.m. of HCO_3^-—which is sometimes the case with certain well water—the water in question is an alkaline water and we must watch out for possible caustic embrittlement. From the point of view of determining the necessary chemical treatment for the water in question, the advantage in using the e.p.m. system is obvious. In the case of the Yangtze water in the winter season, it can be seen from the above e.p.m.'s that the water contains 85 per cent of its total hardness (e.p.m. Ca + e.p.m. Mg = 3.007) as temporary hardness (e.p.m. HCO_3^- = 2.566), and the remaining 15 per cent as permanent hardness, but the amounts are not large and therefore it is a rather soft water for the source of raw feed water supply.

Attempts are often made to express the different constituents dissolved in the water as conventional combinations which would likely exist, if these constituents were present in solid salt form. These are only hypothetical compounds and the results may be different depending on the manner in which these constituents are combined. A general rule, however, may be stated as follows:

   (a) Combine SO_4^{--} with Ca^{++} as $CaSO_4$
   (b) Then combine balance of Ca^{++} with HCO_3^- as $Ca(HCO_3)_2$
            or balance of SO_4^{--} with Mg^{++} as $MgSO_4$
   (c) Next combine balance of HCO_3 with Mg^{++} as $Mg(HCO_3)_2$
            or balance of Ca^{++} with Cl^- as $CaCl_2$
            or balance of Mg^{++} with Cl^- as $MgCl_2$
            or balance of SO_4^{--} with Na^+ as Na_2SO_4
   (d) Finally combine Na^+ (or balance of Na^+) with Cl as $NaCl$

The total of the basic constituents should closely check with the total of the acid constituents, if the analysis was correctly made, unless other acid radicals are present. SiO_2, Fe_2O_3, and Al_2O_3 are generally not combined. The above represents a general practice but the sequence is often modified in special cases where certain other constituents are found to be present.

SCALE FORMATION

As has been mentioned above, scale formation is caused by hardness in the water, particularly calcium sulfate, silica, and calcium hydroxide. While temporary hardness may be removed by heating and thrown down as the carbonate sludge in the preheated feed water, permanent hardness must be removed by chemical treatment. This can be done by means of (a) soda and lime, (b) lime and sodium aluminate, (c) caustic soda and sodium phosphate, or any combination of these, followed by (d) a zeolite treatment, with subsequent addition of a proper amount of trisodium or disodium phosphate or "Akon" to the treated water entering the boilers.

Soda-lime Treatment (Modification of the old Scotch Professor, Thomas Clarke's process)

By treating with lime:
Temporary hardness:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$
$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow Mg(OH)_2 + 2CaCO_3 + 2H_2O$$
$$Fe(HCO_3)_2 + Ca(OH)_2 \rightarrow FeCO_3 + CaCO_3 + 2H_2O$$

Or, on heating,

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O$$
$$Mg(HCO_3)_2 \rightarrow MgCO_3 + CO_2 + H_2O$$
$$Fe(HCO_3)_2 \rightarrow FeCO_3 + CO_2 + H_2O$$
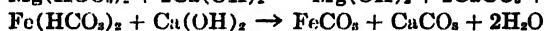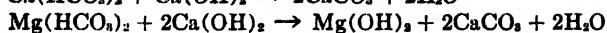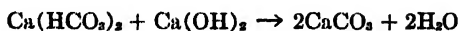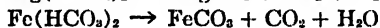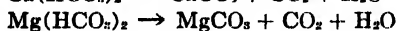
The decomposition of the temporary hardness by heating is rather slow. Hence treatment with lime is often preferred.

Permanent hardness:

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$
$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$$
$$\begin{cases} MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaSO_4 \\ CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4 \end{cases}$$
$$\begin{cases} MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2 \\ CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl \end{cases}$$
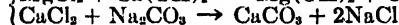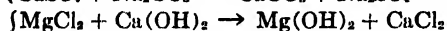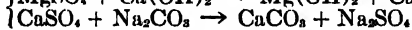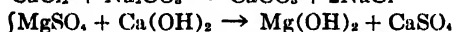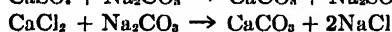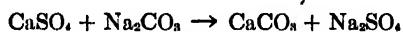
The soda-lime treatment is particularly suitable when water contains larger quantities of non-carbonate calcium and magnesium hardness. Generally speaking, lime need be employed in theoretical quantities, but soda ash added should allow for an excess of about 25 p.p.m.

Lime-Sodium Aluminate Treatment. Sodium aluminate is hydrolyzed to caustic soda and aluminum hydroxide:

$$NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3$$
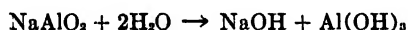
so that the reactions are the same except that aluminum hydroxide sepa-ates out as a voluminous, gelatinous precipitate that serves as a coagulant for the other precipitates. This treatment is economical when water con-tains high temporary hardness, but watch out for residual aluminum in the treated water.

Caustic Soda-Sodium Phosphate Treatment. The reactions are essen-tially the same, sodium hydroxide taking the place of calcium hydroxide. Trisodium or disodium phosphate is used to precipitate calcium, mag-nesium and iron. It is, however, important to observe that when caustic soda is used, no large excess should be taken for treatment. Because of the expensive character of the chemicals, they are often used only for the removal of the last trace of hardness.

$$3Ca^{++} \text{ (or } 3Mg^{++}) + 2PO_4^{---} \rightarrow Ca_3(PO_4)_2 \text{ [or } Mg_3(PO_4)_2]$$
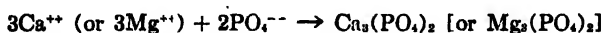
· **Zeolite Treatment.** This treatment removes calcium and magnesium hardness almost completely and can also be used independently when temporary hardness is low. Ordinary zeolite treatment does not remove the carbonates, (CO_3^{--}), does not lower the methyl orange alkalinity, and does not reduce total solids in the boiler feed water so treated. Hence

the zeolite treatment is often used as an after-treatment for one of the above preliminary treatments, (a), (b), and (c), and is itself followed by an acid treatment and degasification to remove CO_2 and to reduce the alkalinity (or pH), as will be seen below. The soda-lime or lime-sodium aluminate treatment does not remove all the hardness, especially in the cold; but it will remove most of the bicarbonates and carbonates. Hence it forms a good combination with the zeolite treatment which forms a subsequent treatment to remove the last portion of the hardness. This combination then gives an excellent feed water with practically zero hardness, but with low carbonates and hence low alkalinity.

The zeolite treatment consists in treating the water by passing it through a thick zeolite bed, generally $3\frac{1}{2}'$-$4'$ thick. The zeolite mass varies from 20 mesh to 40 mesh in size, the "effective size" being about 35 mesh. The zeolites have approximately the composition: Al_2O_3 . Na_2O . $4SiO_2$. $6H_2O$. Both natural and artificial zeolites are employed. When water is passed through a zeolite bed, calcium and magnesium salts are converted into corresponding sodium salts; hence this reaction is known as the Base Exchange Process.

Natural zeolite or Glauconite has a base exchange capacity of **2800-3200** grains of equivalent $CaCO_3$ per cu. ft., and artificial zeolite may have a capacity as much as 7500 grains or more. Natural zeolite in the form of treated "Greensand" of New Jersey, although it has lower base exchange capacity than the artificial zeolite and consequently requires larger bed area, has, however, several advantages: (1) natural zeolite is more durable and is not so likely to disintegrate as artificial zeolite; (2) natural zeolite can stand some turbidity in the water and the bed is not so likely to become plugged by fine silt; and (3) the first cost of equipment, even considering the larger units required, is generally in favor of the natural zeolite. It therefore has a wide industrial application for boiler feed water, whereas artificial zeolite has its field mostly in domestic softening.

It is to be observed that water, after passing through the zeolite bed, contains, besides sodium sulfate and sodium chloride, sodium bicarbonate and carbonate, as mentioned above, in place of the original calcium and magnesium bicarbonates and carbonates. Hence water containing high bicarbonates and carbonates is often not suitable for zeolite treatment directly. For, if zeolite treatment is used directly for water containing high bicarbonates and carbonates, the water may become too alkaline, and sometimes boiler trouble is caused by this, if no correction is applied. For this reason, in the case of very hard water, or water having high temporary hardness, it is often preferred to give the water a preliminary treatment with soda and lime or lime and sodium aluminate, before the zeolite treatment as mentioned above. This has the advantage of neutralizing the acid carbonate in the temporary hardness with lime and throwing the calcium and magnesium down as normal carbonates. For instance,

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$
$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow MgCO_3 + CaCO_3 + 2H_2O$$
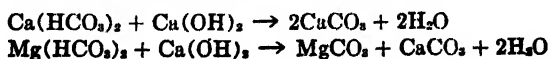
Thus, not only are the calcium and magnesium precipitated, but also the carbonate radical (CO_3^{--}) is eliminated by this treatment. A direct zeolite treatment would simply convert the alkaline-earth bicarbonates to sodium bicarbonate which remains dissolved in the resulting water, giving high pH and requiring large quantities of acid for neutralization. This always results in high soluble solids.

After the water has received a pretreatment with lime and soda, or lime and sodium aluminate, it is settled off and filtered. After filtration the alkalinity in the water is neutralized with sulfuric acid through a feed proportioner with automatic control to keep the pH value between 7.4 and 7.2 for the final zeolite treatment. The water is degasified in wooden or steel tanks; it is then sent through zeolite softeners, and finally to the deaerator and thence to the boilers. This sulfuric acid treatment before the zeolite treatment serves also to adjust the sulfate-to-carbonate ratio so that no treatment after zeolite softening is required. This combination keeps the soluble solids in the water down to a minimum and at the same time removes the objection of leaving high sodium carbonate and bicarbonate in the water after zeolite softening. A small amount of disodium phosphate is then added to the boiler feed to maintain a suitable phosphate content (PO_4^{---}) in the boiler saline.

For the removal of iron, a new zeolite is brought out by the National Aluminate Corporation. This form of zeolite will remove iron and uses salt as the regenerating medium as usual. The mineral is black and of synthetic type. It has a capacity of about 5830 grains per cu. ft., requiring $4\frac{1}{2}$ lbs. of salt per cu. ft. It weighs about 40 lbs. per cu. ft. It has little softening action, but will remove iron, either in soluble iron salt form, or as suspended iron. However, it will not remove manganese.

To a limited extent, iron is also removed by the zeolite treatment, but to remove iron completely, such as in the case where the water is used for caustic manufacture for the rayon industry, a specially treated zeolite such as "Ferrosand" may be employed. "Ferrosand" is made by treating the same natural Greensand with potassium permanganate forming a coating of MnO_2 or Mn_3O_4 on the crystals. These manganese oxides oxidize iron in the water to the ferric state and the Fe_2O_3 is retained on the "Ferrosand" particles mechanically. For regeneration, wash the Ferrosand bed free from Fe_2O_3 by a thorough backwashing at 7-9 gals. per sq. ft. per min., treat the washed mass with dilute $KMnO_4$ solution, and then wash off the excess $KMnO_4$ from the bed. In actual operation, this is done in two stages by treating the water first with Ferrosand to remove iron, then with the ordinary Greensand softeners for softening.

If the zeolite mass for some reason begins to disintegrate, a treatment with a dilute solution of sodium silicate will harden the grain and stop disintegration. After the silicate treatment, the zeolite should be thoroughly washed to get rid of the residual causticity. The base exchange capacity then is temporarily greatly enhanced right after this treatment but will soon become normal. The reaction underlying the silicate treat-

ment is not clearly understood, but it seems that Na_2O rather than SiO_2 is absorbed by the zeolite mass, increasing the activity.

Lime-soda treatment will only reduce the hardness to a minimum of 2-2½ gr. per gal. in the cold, or 1-1½ gr. per gal. in the hot process, without using a very large excess of the reagents in each case; while caustic-soda and phosphate treatment may reduce it to ⅓ gr. per gal. With the zeolite-treatment, the total hardness is reduced to 0.2 or less gr. per gal., although zero hardness is often spoken of in the trade parlance. For this reason, as seen above, the zeolite treatment is used after the lime-soda treatment or lime-sodium aluminate treatment to remove the remaining hardness.

After treatment according to one of the above methods, the water is checked for alkalinity (pH value). For such purpose, a convenient type of the Hellige, LaMotte, or Taylor Comparator may be used, but electrometric methods with the Leeds and Northrup pH potentiometer give more reliable results. If the water is too alkaline (pH value is too high), sulfuric acid is cautiously added to lower the pH value and also to bring up the sulfate content. For this purpose, a sulfuric acid feed proportioner having an electric control, such as made by the American Water Softener Co., or the Permutit Co. or other company may be used. If, on the other hand, the water is not alkaline enough (or pH value still too low), proper amount of caustic soda or soda ash is added to prevent corrosion in pipe lines, economizers and boilers. If the sulfate-to-carbonate ratio after pH adjustment is still not sufficient, sodium sulfate or sodium bisulfite may be added to the treated water in calculated quantities. Lastly, a small amount of trisodium or disodium phosphate is generally introduced to take care of whatever residual hardness there is left in the feed water to the boilers.

To prevent silica scale in the boilers, a certain phosphate concentration (30-50 p.p.m. as PO_4^{---}) may be maintained in the boiler saline. This phosphate constituent has also a great inhibitive effect against caustic embrittlement; but as it is reacted upon by the residual hardness in the water, it is quickly depleted and must be replenished continually. For this reason, in considering inhibitants for caustic embrittlement, only sodium sulfate is considered in figuring sulfate-to-carbonate ratio according to the A.S.M.E. regulations, no allowance being made for the soluble phosphate remaining in the boiler saline.

Silica present in the boiler feed water beyond a half grain per gallon, is considered objectionable, because it forms a glassy, hard scale in the boiler which is particularly objectionable in a high pressure plant. The silica scale is a heat insulator and would cause the front bank of tubes to be burned out or to blister. Silica in water is a troublesome constituent to remove, as it is rather inert and cannot be reacted upon readily by chemicals, producing insoluble sludge. One common remedy, as mentioned above, is to introduce a sufficient amount of disodium phosphate into the boiler feed water. The phosphate then combines with Ca and Mg in the residual hardness, thus avoiding the formation of calcium and mag-

nesium silicates. If a special treatment for silica is desired, the water may be given a pre-treatment with ferric sulfate solution and sulfuric acid to give a pH reading somewhat below 4.0. Then lime is added to bring the pH to around 9.0. This trivalent Fe^{+++} starting from a rather acid condition of $pH = 4.0$ will bring down silica effectively when the water is again made alkaline by lime with an alkalinity around 9.0.* But the simplest way is to use the Akon treatment, or treatment with some form of activated magnesium oxide.

To a certain extent, silica in the water is removed in the hot lime-soda process. This is probably due to the adsorption of silica by the magnesium hydroxide from magnesia introduced with the lime. Magnesia is known to possess the greatest adsorption properties—more marked than ferric or aluminum sulfate—and a method of the removal of silica from the boiler feed water has been devised based on the use of magnesium.** Indeed, for hot removal of silica, Allis-Chalmers Mfg. Co.

Courtesy Betz Laboratories
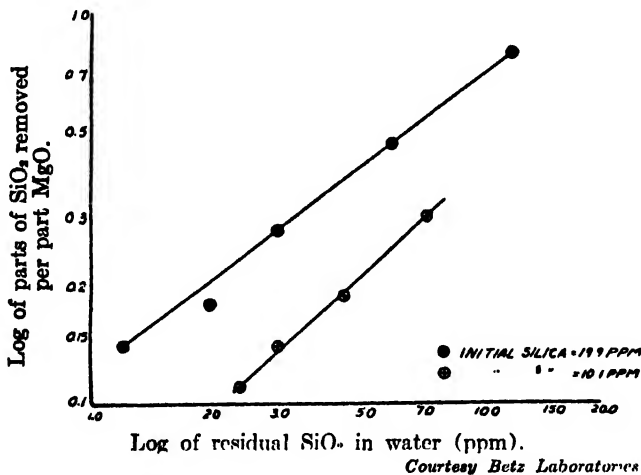
FIG. 105. Relationship between removal of SiO_2 and residual SiO_2 in water.

also put out "Silimite" which is active lime especially burned from dolomitic limestone, and W. H. & L. D. Betz of Philadelphia, Pa., devised an adsorption process with their "Remosil." † This treatment for silica with MgO is best done in the hot solution, say at 90 to 95° C. It can be combined to advantage with the hot treatment of lime and soda ash, so that hardness and silica may be removed in one operation. Loose and light

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* Schwartz, M. C., "The Removal of Silica from Water for Boiler Feed Purposes," *J.A.W.W.A.*, **30**, 659 (1938). Powell, Carpenter, Settar and Coates, "Recent Trends in Water Treatment, *Chem. Met. Eng.*, **46**, 483 (1939).

** Tray, S. W., and Pankey, T. L., "Removal of Silica from Industrial Boiler-Water Supplies," *Combustion*, **12**, No. 5, p. 39 (1940).

† Betz, Noll and Maguire, "Removal of Silica from Water by Hot Process," *Ind. Eng. Chem.*, **32**, 1323 (1940).

grade of MgO removes silica more effectively. Also, a voluminous sludge and prolonged retention provide an intimate contact resulting in a more complete removal.

Figs. 105 and 106 show results of treating silica with magnesia in the field tests made by Betz Laboratories. The relationship shown in the two straight lines in Fig. 105 evidently indicates that the action is one of adsorption * as it conforms to the Freundlich adsorption isotherm of the form

$$Y = KX^n;$$ where Y = Removal of SiO_2 per unit wt. of adsorbing substance.
X = Residual SiO_2 in water.
K and n are constants.

Or, $\log Y = n \log X +$ Const., an equation of a straight line on a logarithmic scale (see Fig. 105).

Fig. 106 shows the decrease of silica in solution with the increase of magnesia by sludge re-circulation.

In the operation of high pressure boilers (above 450 lb. per sq. in. gauge) aluminum in the feed water is objectionable due to the possibility

Fig. 106.

Silica removal by MgO with sludge recirculation.

Courtesy Betz Laborato
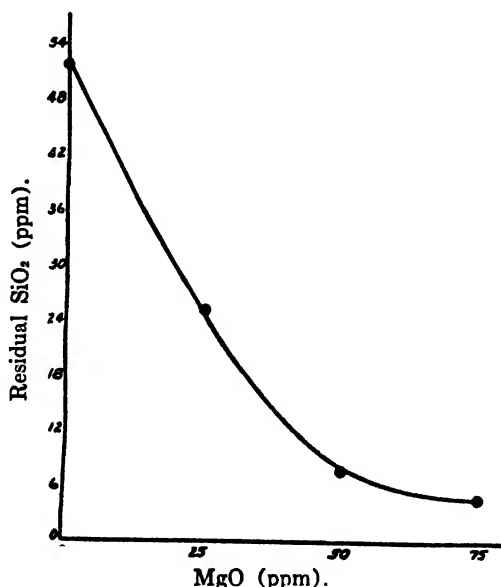
of the formation of Analcite scale with silica on those parts where there is high heat transfer, such as on the water wall tubes. Analcite scale is a double silicate of sodium and aluminum ($Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$) and is formed even when there is no hardness in the boiler, and when a residual phosphate of 40 p.p.m. is maintained. It is a thin, dense scale, possessing high heat insulating properties. If the silica can be kept below 2 per cent of the total solids in the boiler water and the alumina held to

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* Whether it is by adsorption or chemical combination, the sludge formed contains silicates of calcium and magnesium.

about 2 p.p.m., there is usually no trouble experienced. But it is best to keep alumina out of feed water, as much as possible, for high steam pressure operation.

There are cases where alumina cannot be entirely kept out and where silica will run higher than 2 per cent of the total solids. In such cases, the use of Akon (an electric arc dispersion of metallic iron in anhydrous ferrous oxide, which is put out by the Allis-Chalmers Mfg. Co.) will generally remove the silica by adsorption and carry it down as a sludge. The silica can then be kept within proper limits. With the use of Akon the residual phosphate required may be reduced to about 5-10 p.p.m. Akon is in a liquid form and can be fed into the feed water at the intake to the boiler feed pump. The usual dosage is about 3-5 p.p.m. Akon will also reduce foaming and priming (which see) and small amount of oxygen in the feed water, thus helping prevent corrosion in the economizer and boiler.

Residual aluminum in the water from the use of sodium aluminate or aluminum sulfate as a coagulant is objectionable in the rayon-quality caustic manufacture and should be carefully tested and removed. For this reason, coagulation by means of alum should not be carried out in an alkaline condition (*i.e.*, in high pH range).

Raw water often carries considerable mud, such as the muddy water from some rivers. If such water is passed directly through the zeolite bed, the bed will soon be covered with a layer of fine silt and eventually plugged. In such cases, a preliminary treatment of the water by coagulation, sedimentation, and filtration is necessary before zeolite treatment, and this opportunity is afforded by the soda-lime or lime-sodium aluminate pretreatment. However, the zeolite treatment will not permit a hot pretreatment. The temperature of water for zeolite treatment should not exceed 100° F. for natural zeolite and 90° F. for artificial zeolite; otherwise disintegration of the zeolite would result. A brand of specially treated natural zeolite may, however, stand a temperature up to 150° F.

For coagulating the muddy water, aluminum sulfate, sodium aluminate, ferrous sulfate, or lime may be used. Aluminum sulfate may be used in the cold but it reacts much more quickly in hot water. In general, a hot treatment requires less reagents, gives more complete reaction, and takes less time for settling; but the hot process is not suitable for the zeolite treatment as mentioned above. Aluminum sulfate hydrolyzes in water and yields a flocculent precipitate of aluminum hydroxide carrying the fine particles of mud down with it. This reduces the alkalinity and leaves the water acid; neutralization with an alkali is necessary before the zeolite treatment. Sodium aluminate has the advantage over aluminum sulfate because it hydrolyzes to sodium and aluminum hydroxides, leaving the water alkaline. In conjunction with lime for removing temporary hardness, sodium aluminate has been also extensively employed. Ferrous sulfate, upon oxidation to the ferric state, acts like aluminum sulfate and has the advantage of being able to remove dissolved oxygen and silica in the water. Ferric salts act like aluminum salts. Lime has

been found to possess some coagulating properties; but its action is much milder, and much larger quantities would be required. For cold treatment, it may take as much as four times the weight of lime to coagulate the water as the alum. Lime, however, is cheap and is still the best reagent for removing hardness where very hard water has to be treated. Whichever coagulant is used, the water must then be settled and filtered.

Often the coagulating operation and the lime-soda treatment may be done in one step by means of a large sedimentation basin. Excess lime is used in the treatment, together with other reagents, and the water is allowed to settle, recarbonated with CO_2 gas and finally filtered. The recarbonation is done to remove the excess of lime or to convert insoluble $CaCO_3$ to soluble $Ca(HCO_3)_2$ so that it may not deposit itself in the pipe lines or filters later on. This is called "stabilizing" the water, in water works parlance. Very recently, Mr. C. H. Spaulding * of Springfield, Ill., introduced a double-cone "precipitator" (Fig. 107) based on the principle
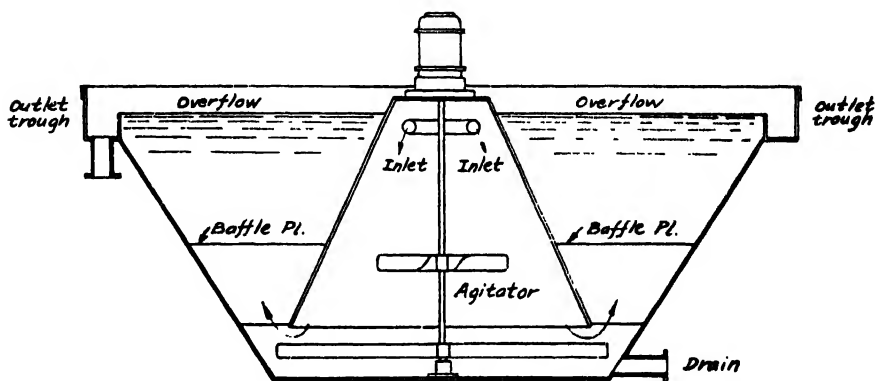
FIG. 107. Spaulding precipitator.

of "hindered settling," using the sludge as its own filtering medium in a conical ring space, the vertical cross-section of which is triangular, with the base line upward. The sludge particles carried up by the upflow of water will distribute themselves evenly at a depth determined by the rate of upflow. The mixing is done inside the central cone, so that water turns upwards around the base of the central cone and flows upward in the sludge filtering space outside. This permits intimate contact of the sludge with the stream of water, and allows time to complete the reaction so that only a very small excess of lime is needed and no recarbonation is necessary. The sloping sides of the sludge filtering space give a larger and larger area on the top, which results in a decreasing rate of upflow (velocity 2" or so per min.), so as to give a maximum settling effect, as the water reaches the surface and decants into a collecting trough. This produces a "stable," clear effluent from the "precipitator" within a minimum detention period of only 45 minutes.

* "Some New Practices in Water Softening," by Chas. H. Spaulding, *Water Works and Sewage*, **85** (March, 1938).

Filtering is generally done in sand filters. For the boiler feed in the ammonia soda plants, many types of filters are on the market, notably the Cochrane filter, International Filter, etc. Such filters may be divided into two main classes: (1) Gravity (or open) filters, and (2) pressure (or closed) filters. In point of construction they may be either vertical or horizontal, cylindrical or rectangular vessels. Pressure filters are gener-
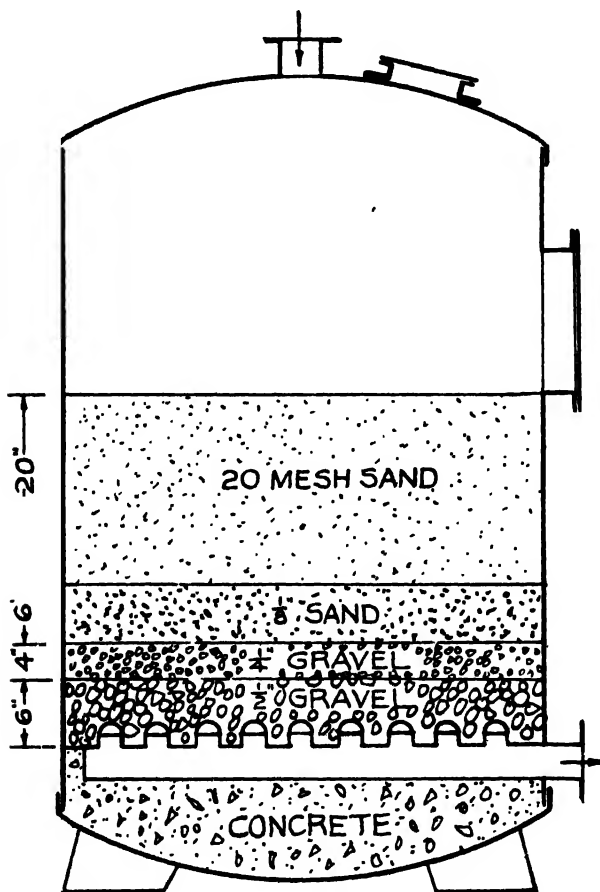
FIG. 108. Vertical cylindrical pressure filter.

ally used in connection with a hot process of softening, and are more desirable where water coming out of the filters has to be lifted to a certain level. This eliminates another boosting pump. The rate of filtration varies from $2\frac{1}{2}$-4 gal. per min. per sq. ft. of filter bed, depending upon the uniformity of the sand and gravel particles, the condition of the filtering medium, and the thickness of bed. It pays to select the coarsest sand available (1-1$\frac{1}{4}$ mm. size of sand is best) for the filtering medium; and then it is possible to filter at the rate of 4 gal. per min. per

sq. ft. filter area. One construction of a vertical cylindrical pressure filter and one construction of square concrete open filter are shown in Figs. 108 and 109. Open (gravity) filters are, however, often preferred by some users because of simplicity in backwashing and in general maintenance. As can be seen, the construction of the open filter is exactly the same as that of the closed filter, minus cover over the top for gravity flow. Both pressure and gravity filters must be washed frequently (once in every 8 or 12 hours) by backwashing with water at the rate of about 9 gal. per min. per sq. ft. of filter area. If the sand is very coarse, it is possible and also advisable to backwash at the rate as high as 20 gal. per min. The washing of gravity or open filters may be aided by blowing compressed air into the filter or spraying the surface layer of sand by means of high-pressure water sprays to break up the surface crust or
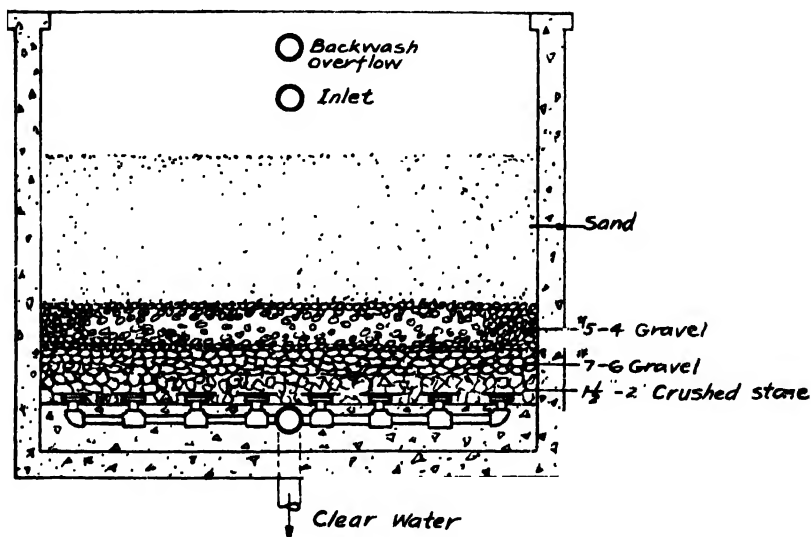
Fɪɢ. 109. Open concrete filter.

"mud balls." For the filtering medium, many substances have been used: calcite, magnetite, activated carbon, anthracite ("Anthrafilt"), gravel, sand, etc.; but in the hot softening process where hot water carries considerable alkalinity, a silicious filtering medium, such as sand, should be avoided because of the tendency of the alkaline hot water to attack the silicious material. This may increase silica content in the water. In such cases, magnetite may be substituted.

Activated carbon has recently also been used as a filtering and purifying medium. Incidentally, this also removes color and taste from the water. Its use for the filtration of water after alum or aluminum sulfate coagulation is found also to reduce the residual content of aluminum in the resulting water, which is most desirable for the manufacture of rayonquality caustic soda (see Chapter XIX).

The rate of percolation of water through the zeolite bed varies from 2 to 3 gal. per min. per sq. ft. of bed area. The pressure drop through the bed $3\frac{1}{2}'$-4' thick amounts to 2-5 lbs., depending upon the condition of the bed and the volume of flow. The time of contact of water with the zeolite mass is estimated at from 4 min. (for a rather soft water) to 10 min. (for a hard water). When some residual hardness in the effluent begins to show, it is time to regenerate the zeolite bed by means of strong brine containing low calcium or magnesium. This is done generally once in 24 hours of operation. For ordinary zeolite softeners using down-flow of water, an upward stream of washing should precede the brine regeneration. An upflow of wash water of about 7 gal. per sq. ft. of area is generally sufficient. Care should be exercised not to allow the upward stream of washing to attain so high a velocity as to cause loss of zeolite carried over by the water. The whole regeneration operation takes 30 to 45 min. depending upon the physical characteristics of zeolite, porous zeolite taking a somewhat longer time for regeneration. Regeneration takes $1\frac{1}{2}$ to $2\frac{1}{2}$ lbs. of good salt (containing low Ca and Mg) per cu. ft. of zeolite, depending upon the base exchange capacity of the zeolite in question. This corresponds to one-half pound of salt per 1000 grains (kilograins) of hardness as $CaCO_3$. The time of actual contact of the brine with the zeolite mass varies from 10 to 20 minutes, depending upon whether the zeolite in question reacts on the surface only or is porous and active throughout the mass. An average of about 15 min. of contact is sufficient to effect the reaction. As a rule, artificial zeolite is more porous than natural zeolite (Greensand or Glauconite), and hence has a higher exchange capacity and takes a somewhat longer time to regenerate. The bulk density of artificial (synthetic) zeolite is 50 to 55 lbs. per cu. ft., whereas that of the natural zeolite is 90 to 95 lbs. The heavier zeolite has less tendency to be washed away during back-washing. Synthetic zeolite is made from sodium silicate and an aluminum compound into a gel form, called zeolite gel, which is then dried to a hard granular material. The ordinary zeolite softeners are arranged for downflow, *i.e.*, the water to be softened enters at the top, flows through the zeolite bed, and passes out at the bottom of the softener, the gravel bed being located at the bottom to support the zeolite bed. Sometimes, where a high rate of flow through the softener is desired, in order to avoid excessive pressure drop through the zeolite mass, an upflow softener is employed in which the water is passed in through a manifold at the bottom and flows out from the top of the softener, the construction of the softener remaining essentially the same. This incidentally does away with the necessity of back-washing of the zeolite mass before each regeneration. The danger to be observed in this arrangement is the possible loss of zeolite particles floating off with the upflow of water from the top of the softener, if the upflow velocity through the softener should become excessive. To overcome such an objection, a two-flow pair of softeners is installed, and water is passed first into the upflow unit, flows into the top of the downflow unit and out at the bottom. Thus, any zeolite particles floating out

from the upflow unit would be caught in the downflow unit, Fig. 110. Here the two units are connected in series, but the pressure drop through the two units in series will by no means be small. Such are the details of the arrangement and design of the zeolite softeners, and will not be further dealt with.

Some recent installations have used zeolite equipment operated entirely automatically by an electric control mechanism. Some saving in salt and labor is claimed. A simple device has also been worked out whereby spent brine from regeneration may be partially recovered and strengthened for use.

Courtesy Elgin Softener Co.
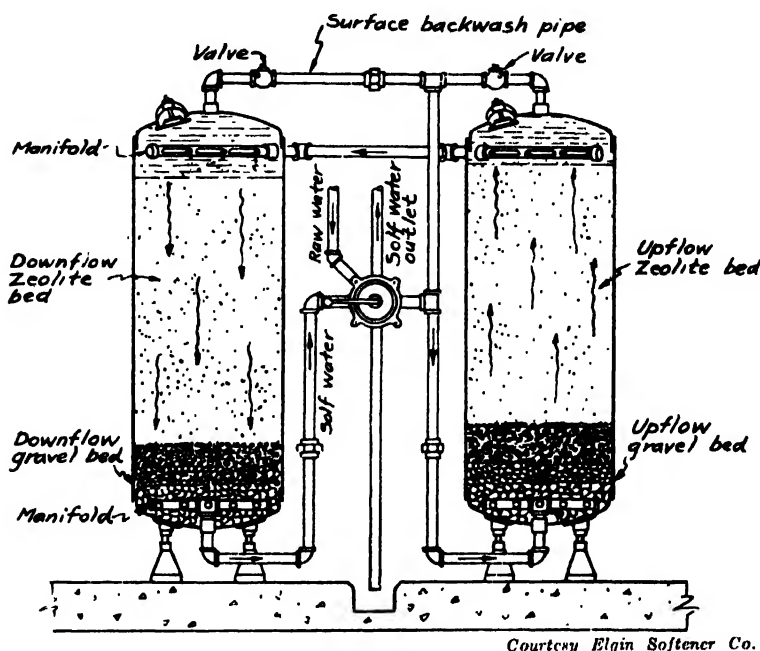
FIG. 110. "Two-Flo" softener.

As a recapitulation, we may say that the zeolite treatment, while excellent in removing practically all the hardness in the water for boiler feed, does not reduce the total solids and often aggravates the alkalinity situation in the feed water. It is often not suitable for direct treatment when water contains high sodium bicarbonate or when water is high in temporary hardness or carbonate hardness, without lime pre-treatment to get rid of most of the temporary hardness. Then also the zeolite treatment must be preceded by an acid treatment (usually sulfuric acid) to neutralize excess lime and excess alkalinity, and followed by neutralization and aeration. But then total solids in the feed water are increased considerably, especially when it is necessary to maintain the sulfate-to-carbonate ratio according to the A.S.M.E. regulation.

A rather recent development is the use of hydrogen zeolite, such as "Zeo-Karb H" * of the Permutit Company. This hydrogen zeolite is not really a zeolite in the chemical sense, but on account of its similarity in the manner in which it is used, it is referred to as a "zeolite." It is made by sulfonating and granulating bituminous coal or other carbonaceous material in a manner somewhat similar to the preparation of activated carbon. Hence it is classified as carbonaceous "zeolite." † It can be regenerated either with a mineral acid (sulfuric acid) or with salt; in the latter case it performs exactly the same as the synthetic or natural zeolites. The Permutit Company refers to the former process as "Zeo-Karb H" and the latter as "Zeo-Karb Na." For generality, we shall call the former the hydrogen exchanger and the latter the sodium exchanger as being more descriptive of their properties. This carbonaceous granule is coarser than natural zeolite and therefore can handle high rates of flow of water through the softener (6–7 gal. per min. per sq. ft. of bed area with the same pressure drop). One remarkable property is that it can replace sodium, when it is used as the hydrogen exchanger and regenerated with acid. When used as the sodium exchanger, its base exchange capacity is 5000–8000 grains of $CaCO_3$ per cu. ft., which is almost as high as the capacity of a synthetic zeolite. It will take 2–4 lbs. of salt per cu. ft. of the volume of sodium exchanger. As the hydrogen exchanger, it will replace all metallic cations, Ca^{++}, Mg^{++}, Fe^{++}, Na^+, etc. by hydrogen, has a capacity of 8000–9000 grains per cu. ft., and will take $2\frac{1}{4}$–3 lbs. of 66° Bé. sulfuric acid per cu. ft. If we let R represent the anion, M the cation and HZ the hydrogen exchanger,

$$MR + HZ \rightarrow MZ + HR$$
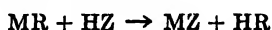
When $R = SO_4^{--}$, Cl^-, CO_3^{--}, HCO_3^- or NO_3^-, we have, after treatment, H_2SO_4, HCl, H_2CO_3, or HNO_3, respectively, in the water. For boiler feed water or for any industrial purposes, these free mineral acids must be neutralized back by an alkali, when sodium ion (Na^+) will be restored, and there seems to be no gain in this respect over the ordinary zeolite treatment. But the advantage consists in converting the bicarbonates and carbonates into free carbonic acid which may be easily liberated from water by degasification without any acid treatment,

$$H_2CO_3 \rightarrow CO_2 + H_2O$$

whereas in the ordinary zeolite treatment, all calcium and magnesium bicarbonates and carbonates would be converted into the corresponding sodium bicarbonate and carbonate which can only be decomposed by adding a mineral acid such as H_2SO_4. In this way, in the ordinary zeolite-treated water, sodium bicarbonate and carbonate would be con-

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* Applebaum, S. B., and Riley, R., "Zeo-Karb H—A New Method of Conditioning Water to Remove Sodium Bicarbonate Chemically Instead of by Distillation," *Ind. Eng. Chem.*, 30, 80 (1938). Also, Applebaum, S. B., "Applications of Carbonaceous Zeolites to Water Softening," *J.A.W.W.A.*, 30, 947 (1938)

† Tiger, H. L., "Carbonaceous Zeolites—An Advance in Boiler Feed-Water Conditioning," *Trans. A.S.M.E.*, 60, 315 (1938).

verted by the acid into sodium sulfate, remaining as a soluble solid in the feed water, and consequently the total solids are increased.

In actual practice, these free mineral acids may be neutralized after the hydrogen exchange by mixing the effluent from the hydrogen exchanger unit with the effluent from the ordinary zeolite softeners in a proper proportion to remove the acidity or to obtain any desired alkalinity in the mixture. Thus, total solids in the feed water are reduced and the alkalinity can be regulated to any desired degree by the combination of the hydrogen exchanger unit with a sodium exchanger unit or with an ordinary zeolite softener. The hydrogen exchanger is especially good for certain artesian well water containing high alkaline carbonates (sodium bicarbonate mostly) having low permanent hardness; in which case a calculated amount of the raw water may be by-passed from the hydrogen exchanger unit and mixed with the effluent from the unit to neutralize its free acidity. Also, the hydrogen exchanger is very good for water containing high temporary hardness because the carbonic acid formed in the resulting water may be driven out by degasification, with the result that no alkali neutralization is needed. This carbonaceous mass, not being a silicious compound, offers absolutely no danger of increasing the silica content of the water treated with it. However, the fact that the hydrogen exchanger will replace sodium ions as well, thus converting sodium sulfate, sodium chloride or sodium nitrate in the water into corresponding sulfuric acid, hydrochloric acid and nitric acid, has no significance, because such free mineral acids in the treated water would have to be converted into sodium salts again before the water is fit for use in the boilers.

Still another good combination is to use cold lime treatment, employing a moderate excess of lime and soda ash, and then follow it with the hydrogen exchanger treatment, by-passing a proper portion of the water for neutralizing the free acidity in the effluent from the hydrogen exchanger unit. This gives low total solids and permissible amount of the remaining hardness for the boiler feed, while the alkalinity can be regulated to any desired pH reading. This combination is applicable to any kind of water where the non-carbonate hardness is high.

Before the advent of the hydrogen exchange process, the reduction of the excess of the bicarbonate (and carbonate) in the feed water was effected wholly by lime treatment before zeolite treatment. Then, in order to bring the sulfate-to-carbonate ratio to the A.S.M.E. specification after the zeolite treatment, sulfuric acid or sodium sulfate is added to the zeolite-treated water in predetermined quantities. Now with the advent of the hydrogen exchange process, it is possible to maintain this A.S.M.E. sulfate-to-carbonate ratio by eliminating the bicarbonates (and carbonates) in the water instead of adding sodium sulfate or sulfuric acid, thus keeping the soluble salts in the feed water at a minimum.

To summarize, the advantages of the hydrogen exchange or Zeo-Karb H process may be stated as follows:

A. Removal of Na as well as Ca, Mg, Fe, etc.
B. Decomposition of sodium bicarbonate or carbonate by this treatment and subsequent degasifying.
C. Reduction of total solids to a minimum.
D. Freedom from silica contamination when low-silica water is desired.
E. High exchange capacity (5-8 kilograins per cu. ft.) and high rate of water flow through the bed at 6-7 gals. per sq. ft. area.

Its application is of particular interest in boiler plants,

a. Where distilled water would be required for the make-up, as in the case of high-pressure and high-temperature steam generators.
b. Where water available is the artesian well water containing high alkaline bicarbonate and carbonate.
c. Where combination of other process or by-passing of the raw water can be utilized for the neutralization of the free mineral acids in the treated water.
d. Where the feed water available contains very high carbonate hardness or very high temporary hardness.

Recently synthetic resins have been developed for application to water softening and are found to possess good base-exchange (cation-exchange) properties. These base-exchange resins are prepared from phenolic compounds or tannins, by condensation with an aldehyde (formaldehyde, acetaldehyde, etc.) in the presence of concentrated hydrochloric acid, and are used in the same way as the zeolites. They are then regenerated with salt (sodium chloride) or hydrochloric acid. By the use of selective resins, practically all metal ions present in the water—not only calcium, magnesium, iron, manganese, etc., but also sodium, potassium, ammonium, aluminum, lithium, etc—may be removed and replaced with sodium or hydrogen ion, so that either their sodium salts or their corresponding free acids are formed in the water.

Most interesting is the behavior of the commercial sulfited tannic extracts (such as quebracho extract, catechu extract, chestnut extract, or hemlock cellulose sulfite extract) which, when insolubilized by heating to 80° C. with 4-5 per cent of concentrated sulfuric acid, or with petroleum acid sludge, and then washed and dried, yield an insoluble mass possessing even higher base-exchange properties than the phenolic or tannin-aldehyde resins, and much higher base-exchange capacity than the Greensand. Further, the base-exchange capacity is not lowered by low pH (or acid) condition, nor is the mass attacked by dilute mineral acids, in the same way as the Greensand or the gel zeolite is attacked.

On analogy to the zeolite, Carleton Ellis termed those resinified organic bodies, "organolites." *   As water-softening agents, they possess many

* Burrell, H., "Organolites (Organic Base-Exchange Materials)," *Ind. Eng. Chem.*, **30**, 358-363 (1938).

advantages over the ordinary zeolites in that (1) they have a high base-exchange capacity, (2) they are less affected by acid or alkaline conditions in the water, (3) they may be regenerated either with sodium chloride or with hydrochloric acid, if desired, so that either the sodium salts or corresponding acids are formed in the water so treated, and (4) they may stand hot water almost up to the boiling point without disintegration. As mentioned in connection with Zeo-Karb Na and Zeo-Karb H, a combination of salt-regenerated resin treatment with acid-regenerated resin treatment may be employed; or a suitable portion of raw water may be by-passed and mixed with a stream treated by the acid-regenerated resin for bicarbonate removal and alkalinity control. This method is especially adapted to the treatment of certain alkaline waters which contain excessive sodium bicarbonate and carbonate, or to a kind of hard water whose hardness consists of essentially calcium or magnesium bicarbonate (practically all temporary hardness). The bicarbonate or CO_2 in the resulting water is simply removed by aeration, as has been pointed out before.

On the other hand, certain aromatic amines (such as aniline, phenylene-diamines, toluidines, etc.) may be similarly resinified by an aldehyde and found to possess acid-exchange properties. They will remove acid radicals, such as SO_4^{--}, Cl^-, NO_3^-, etc., from water, and may be regenerated by a solution of ammonia, sodium hydroxide, sodium carbonate or sodium bicarbonate. By first removing the metal (cations) from the water with acid-regenerated resin as mentioned above, and then removing the acid radicals in this way, it is possible, by repeated treatment, to reduce the total soluble salt content in the resulting water to 1 ppm.[*] The cost of getting a practically distilled water from sea water by this method would be considerably below that of distillation. The study was made in the Chemical Research Laboratory, Teddington, England, in 1934-6 and in subsequent years, and has aroused considerable interest in the field of water purification.[†]

It would be beyond the scope of this book to go into the many interesting details regarding these synthetic resins, except mentioning that the base-exchange property of the phenolic or tannin-aldehyde resins or of tannin-acid sludge-insolubilized bodies seems to be due to the presence of the hydroxyl group (OH) or sulfonic group (HSO_3). The size of particles of these organolites is about the same as that of the ordinary zeolite (through 20, on 40 mesh) but they are lighter than Greensand, the bulk density being about 45-50 lbs. per cu. ft., which is of the order of the bulk density of the synthetic zeolites (alumino-silicates).

It may be further remarked that all the above non-siliceous "zeolites," even when used only as a base exchanger using salt regeneration may sometimes be preferable to Greensand or gel zeolite because they do not cause increase in silica content in the water so treated. Silica, however, is not removed by these resins and must be first removed by other means.

[*] Goudey, R. F., "Removal of Salts from Water," *Journal A.W.W.A.*, **32**, 435 (1940).
[†] Adams, B. A., and Holmes, E. L., "Absorption Properties of Synthetic Resins," *J. Soc. Chem. Ind.*, **54**, 1-6 T (1935).

Excessive Concentration of Soluble Solids

The first effect of a high concentration of soluble matter on the boiler water is foaming and priming; these may also be caused by high suspended matter as well as high soluble solids, and sometimes also by the presence of oil in the water. Accumulation of soluble matter in the boilers is brought about by high soluble matter carried in the feed water and by the high rate of evaporation in the boilers, when the rate of blow-down becomes inadequate. When the engines and turbines run condensing, the situation is not so serious; but, when something like 100 per cent make-up water is required daily as in the ammonia soda works, the remedy may be costly, if no other source of water is available. For only through distillation by means of an evaporator could these soluble solids of alkali salts be eliminated. One remedy is to install a continuous blow-down for the boilers. This provides heat recovery for heating the feed water, using a flash tank and heat exchanger for this purpose. This continuous blow-down system works very smoothly and keeps steady load and pressure conditions in the boilers.

As mentioned above, there is a kind of artesian well which contains high soluble salts but very little hardness in the form of Ca or Mg salts. Fortunately, this kind of water frequently contains high alkaline carbonates (mostly as $NaHCO_3$) and the modern hydrogen exchanger (see above) is able to eliminate these soluble alkaline carbonates without neutralizing the water with an acid.

When the suspended matter accumulates so fast that blow-down becomes inadequate to prevent accumulation, especially when some internal treatment is carried on, it is best to install a sludge "De-concentrator" so that the boiler saline may be passed through the "De-concentrator," the clear water returned to the boiler, and the concentrated sludge drained out at intervals. A notable type of such equipment is that manufactured by the Elgin Softener Corporation of Elgin, Ill., specially recommended where a certain amount of raw water has been by-passed and fed to the boiler along with the treated water; thus some internal treatment is effected in the boiler. For this purpose, a predetermined quantity of the boiler saline is circulated continuously through the "De-concentrator" installed outside the boiler, where the mud and sludge are separated and the clear water is returned to the boiler. Circulation is continuous and automatic and is done without loss of heat. The quantity of water circulated is proportioned according to the amount of suspended matter in the saline. Here this equipment will perform more advantageously than the continuous blow-down.

Foaming and priming depend upon many factors. While the chief cause may be excessive concentration of suspended and soluble solids, the phenomena also depend upon (1) the construction of the steam drum, the method of circulation of the water in the boiler, and the amount of steam space in the steam drum; (2) the presence of oily matter, organic matter or high alkalinity; and (3) the non-uniformity (or irregularity) of steam

drawing and furnace firing. The American Railroad Chemists have rated the foaming qualities of water on the basis of concentrations of soluble salts, as follows (expressed in parts per million):

TABLE 139. Foaming Grading of Raw Waters for Boiler Feed.

Soluble Salts (ppm.)	Grading
120 or less	Excellent
120 to 260	Good
260 to 430	Fair
430 to 700	Bad
700 and up	Very bad

This is merely an attempt to classify water as regards its foaming tendency, and is, of course, subject to difference in individual experience and opinion. In general, with the ordinary water-tube boilers operating at low or moderate pressures, when a concentration of 4000 ppm of total soluble solids in the boiler saline is reached, foaming difficulties begin to show. If the concentration is increased beyond this figure, water level appears unsteady and priming out of the stop-valve is generally observed. If for some reasons the concentration of total solids reaches 9000 ppm, because of increase in the viscosity of the water in the boiler, serious local heating may occur and tube rupture may result. For modern high-pressure boilers, this situation is greatly aggravated and the tolerable limit of total solids in the boiler saline is much lower.

CORROSION AND PITTING

Corrosion and pitting in the boiler tubes and on the drum plate or rivet heads are caused by dissolved oxygen in the feed water or by dissolved CO_2 from $NaHCO_3$ present. If the water has a low pH value or if it contains some acidic salts, such as $MgCl_2$, $CaCl_2$, etc., serious corrosion will occur, if the acidity is not removed. Consequently, modern steam boilers call for a feed water carrying a distinct excess of alkalinity to the extent of 10-15 ppm (calc. as $NaOH$) with a pH value of 8.5-9.0 on leaving the feed-water heater. Corrosion may be found in the steam space in the economizer, or around the tube edges, or in the lower end of the tube opening, or on the rivet heads above the water line. But sometimes it occurs on the drum plates under the water line, and may be observed also at the lower half of the mud drum as light brown spots with numerous depressions on the surface.

A zeolite-treated water is often found to possess marked corrosion properties. This is due to its low or zero hardness and the absence of any coating formed inside the boiler. The zeolite treatment being made in the cold, the water may contain oxygen to the extent of 7-8 cc. per liter and much of the dissolved CO_2 in the form of sodium bicarbonate. Unless the feed water is acidified, degasified, heated, and deaerated in the neighborhood of 212° F., much of the oxygen and CO_2 will find their way to the economizer and to the boilers. Fortunately, nowadays a combination

of feed water heater and deaerator is a standard equipment, and practically all the oxygen may be driven out (to less than 0.03 cc. O_2 per liter) in the deaerator if operation is carefully controlled. However, if corrosion still persists, it is necessary to add some sodium sulfite (Na_2SO_3) to the feed water after deaerating, and maintain its pH value at 8.6-9.0. The sodium sulfite will reduce oxygen and form sodium sulfate. The Na_2SO_3 solution may be added by means of a small plunger pump into the suction of the feed water pump. It is very essential to add the solution uniformly to the stream of the feed water on its way to the boilers. Fig. 111 shows the relationship between the water temperatures in the deaerating
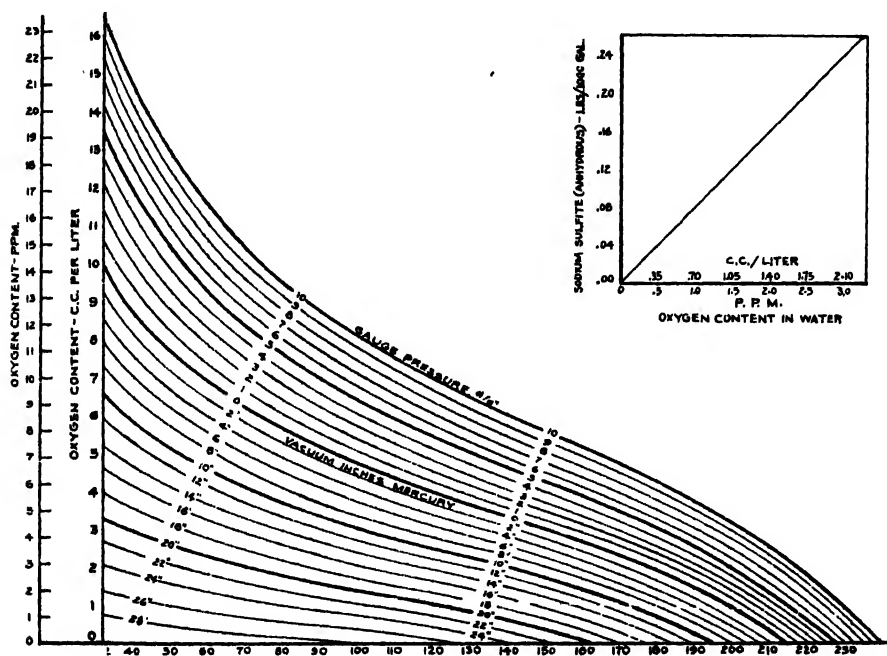
Courtesy The Cochrane Corporation

FIG. 111.   Relationship between temperatures and oxygen dissolved in water.

heater and the oxygen content in the boiler feed water under various pressure and vacuum conditions in the heater. On the same figure are shown quantities of anhydrous sodium sulfite to be added to the water for the removal of oxygen (if desired) corresponding to the oxygen content in the water.

Sometimes corrosion in the boiler is attributable to the presence of fatty acids from the compounded cylinder oil in the exhaust steam of the engine-driven CO_2 compressors, air compressors, pumps, etc. Oil in general should not be present in the feed water, no matter whether it is an animal oil or mineral oil. If it is present in the exhaust steam intended for boiler feed, the steam should be led through an efficient oil separator

and filter. If it is in the condensate, treatment with aluminum sulfate and soda ash followed by decantation may be resorted to, to remove the oil before the condensate is returned to the boiler. If steam turbines are used to drive generators, water pumps, gas compressors, etc. in an ammonia soda plant, no oil will be present in the exhaust steam.

It should be observed that most of the CO_2 comes from sodium bicarbonate and sodium carbonate present in the feed water which has not been properly acidified and degasified. In the boilers all the sodium bicarbonate is decomposed to normal sodium carbonate:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2 \text{ at about } 212° \text{ F.}$$

and, further, the normal carbonate then is decomposed or hydrolyzed to caustic soda.

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2 \text{ at about } 380° \text{ F.}$$
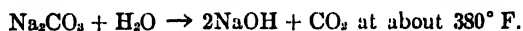
The latter reaction, or hydrolysis, occurs to the extent of about 30 per cent of the total sodium carbonate present in low-pressure boilers, but may be as high as 80 per cent in higher-pressure boilers. CO_2 gas so liber-
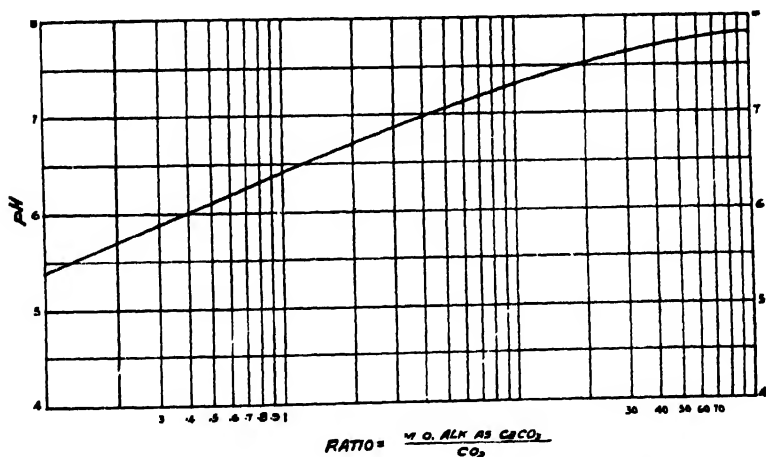
Fig. 112. Curve showing pH values vs. ratio of methyl orange alkalinity in feed water.

ated comes out with the steam and finds its way to the exhaust steam and condensate. Such CO_2 gas present in the steam causes corrosion also in the steam main and steam piping. The steam condensate which is to be returned to the boilers may then contain considerable free CO_2 and become corrosive. In ammonia soda plants where exhaust steam is used for heating, distillation or evaporation, low CO_2 in the exhaust steam and in the condensate for the boiler feed is desirable. If the feed water to the boilers carries low alkalinity and has been properly degasified, there will be little CO_2 generated in the boilers, and hence low CO_2 in the exhaust steam or in the condensate. The presence of free CO_2 in the condensate

may be determined by its pH value as shown in Fig. 112,* which shows the relationship of pH readings to the ratios of the methyl orange alkalinity (calculated as $CaCO_3$) to free CO_2 in the condensate.

CAUSTIC EMBRITTLEMENT

For more than three decades boiler failures have been recorded when feed water from some deep wells carrying high alkalinity, or when zeolite-treated water, or feed water overtreated with lime and soda, was used in the boilers. Cracks occurred along riveted seams; upon examination these were found to be inter-crystalline. It was found that in all boilers that failed this way, the water in the boilers carried high caustic alkalinity and the concentration of sodium sulfate in the boiler saline was low; and that, on the other hand, where a certain amount of sulfate existed, no such trouble occurred. Prof. S. W. Parr and F. G. Straub of the University of Illinois conducted many investigations and found that besides the sulfate (SO_4^{--}) other acid radicals such as PO_4^{---}, CrO_4^{--}, and even CO_3^{--} also had such inhibitive properties, the soluble PO_4^{---} being most effective —many times as effective as the SO_4^{--}. The A.S.M.E. recommends that the ratio of sodium sulfate to the total alkalinity calculated as Na_2CO_3 be maintained in the boiler saline as follows:

TABLE 140. A.S.M.E. Recommendations of Sulfate-to-Carbonate Ratio.

Boiler Working Pressure	Sodium Sulfate Total Alkalinity as Na_2CO_3
Up to 150 lbs. gauge	1
150 to 250 " "	2
250 to 600 " "	3

Above 600 lbs. only distilled water from an evaporator should be used for the small make-up required. Ordinarily, sodium sulfate is the inhibiting agent used, although nowadays phosphate in the form of tri- or disodium phosphate has also been used extensively. At or above 600 lbs. pressure, the addition of such an amount of sodium sulfate may not be tolerated, but tri- or disodium phosphate can be used in much smaller quantities (40 ppm.) for the same purpose. The phosphate, however, is likely to be depleted by uniting with the residual hardness in the water and precipitated as insoluble phosphates of calcium, magnesium, or iron in the boiler. Prof. F. G. Straub of the University of Illinois gives the following curves in terms of the ratios of $Na_2CO_3/NaOH$ as ordinates and $Na_2SO_4/NaOH$ as abscissas.† Points lying to the right and above the curves are considered safe for the respective pressures in question. If we considered sodium carbonate left undecomposed in the water as also contributing the inhibiting properties, the ratio of the sum of sodium sulfate and sodium carbonate to sodium hydroxide equivalent to $2\frac{1}{4}:1$ or higher

* "Treatment of Boiler Feedwater by Zeo-Karb Process" by J. D. Yoder, *Combustion*, May, 1939.

† "Embrittlement in Boilers," University of Illinois Bulletin No. 216 by Frederick G. Straub, p. 77 (modified slightly from original).

(as shown by line MN, Fig. 113) would seem to be safe for all ordinary pressures, especially when phosphate is also present in the boiler saline. Thus,

$$\frac{Na_2SO_4 + Na_2CO_3}{NaOH} \lessgtr 2.5$$

$$\frac{Na_2SO_4 \cdot Na_2CO_3}{NaOH} \gtrless 2.5$$
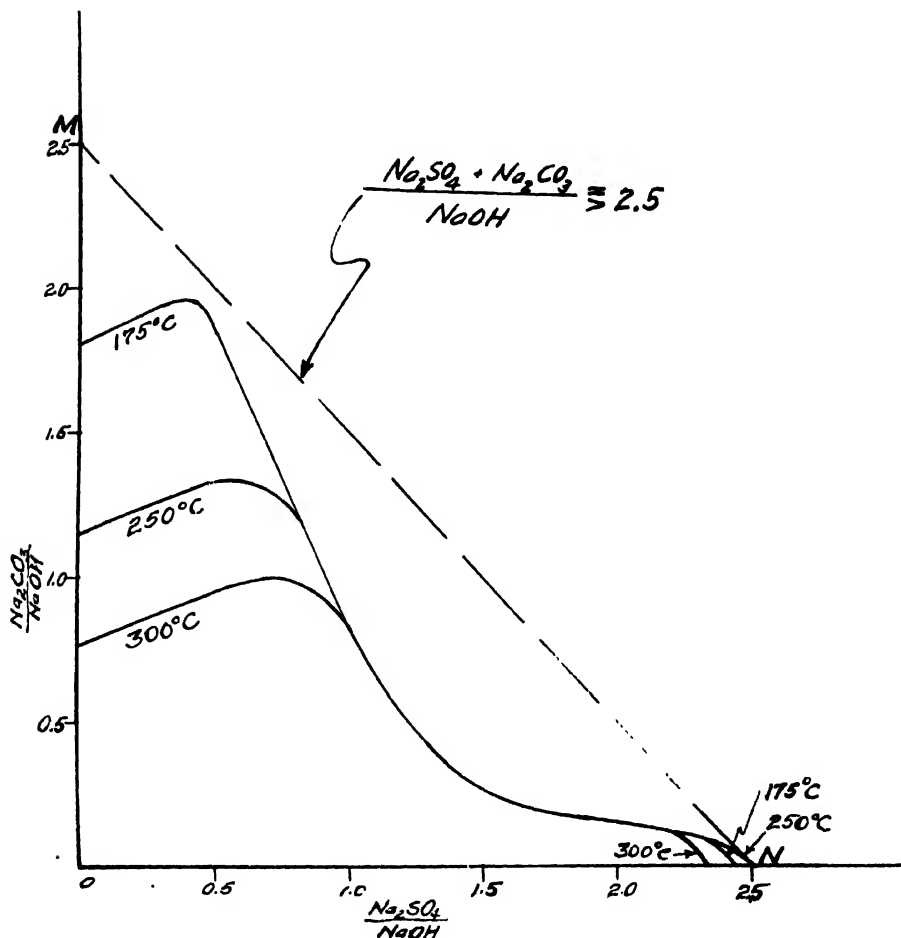
FIG. 113. Curves showing ratios $\dfrac{Na_2CO_3}{NaOH}$ to $\dfrac{Na_2SO_4}{NaOH}$ in boiler water to prevent caustic embrittlement.

Of course, if the boilers are electrically welded, as is at present carried out under Class I Welding with X-raying and annealing, the danger of caustic embrittlement *a priori* will be practically eliminated.

The following figures are given as a guide to the boiler operation under working pressures between 300 and 600 lbs. per sq. in. gauge in ammonia soda plants:

TABLE 141. Conditions for Boiler Feed Water.

1. Alkalinity: 15 ppm as Na_2CO_3
2. Total solids: less than 100 ppm
3. Dissolved oxygen: less than .03 cc. per liter
4. Sulfate-to-Carbonate ratio: 3:1 (unless the drums are all welded)
5. pH from deaerator to boiler: 8.7 (or 9.3 if an economizer is used)
6. Total hardness: less than 1.0 grain per gal.
7. Total silica: less than 6 ppm as SiO_2
8. Oil: nil

TABLE 142. Conditions of Boiler Saline (Internal Water in Boiler).

1. Causticity: less than 200 ppm as NaOH
2. Total solids: less than 1500 ppm
3. Sulfate-to-Carbonate ratio: 3:1 (unless the drums are all welded)
4. Phosphate excess in solution (in boiler saline): 35-45 ppm as PO_4^{---}
5. Oil: nil
6. CO_2 present in steam generated: less than 10 ppm
7. Total silica: less than 30 ppm as SiO_2

The pH value in the raw water is 7.0. That of the water coming from the zeolite tank may be 7.2-7.4 . That in the feed water heater or deaerator is usually increased as the result of the loss of CO_2 by the decomposition of the bicarbonate and may be from 8.6 to 9.0, while that of the water inside the boilers taken from the blow-off (boiler saline) may be as high as 11.0 with sulfate-to-carbonate ratio of 3 to 1 or higher.

TREATMENT OF COOLING WATER

Cooling water in ammonia soda plants, as a rule, does not receive any chemical treatment, except in a very special case where the only source of cooling water available is too hard or too corrosive for the apparatus and piping. Ordinarily, cooling water should be cold and clean or clear. If it is turbid or muddy, it should be settled or filtered. Cooling water for ammonia soda plants usually comes from deep artesian wells because of its low temperature and of its constancy in temperature all the year around, summer and winter. The requirements for cooling water for ammonia soda plants are:

(a) Low temperature
(b) Clearness and cleanness (freedom from excessive suspended matter or mud)
(c) Freedom from scale formation
(d) Freedom from corrosive properties

In addition to the low temperature, especially during summer, and freedom from the excessive suspended matter or mud, the water must not form scale coating in the cooling pipes or in the coolers or condensers; otherwise the rate of heat transfer would soon be greatly lowered. Generally, if the cooling water contains much hardness or possesses scale-forming properties, scale or incrustation will build up in the pipe sections at the exit end or on the cooling surface in the hot portion of the apparatus. This not only cuts down effective cooling but may also constrict passage of water through the cooler. If the hardness is mostly tem-

porary, the trouble may be avoided by treatment with lime followed by settling. If the cooling water contains high permanent hardness, such that it forms hard scale in the pipes and apparatus, lime-soda treatment, as described under boiler feed-water treatment, may be employed; but this is seldom found necessary. If the cooling water contains much acidic salts and is therefore corrosive, lime treatment with or without soda ash will remove the acidity and corrosive properties. If the cooling water in question causes much algae growth that interferes with effective heat transfer, treatment with copper sulphate, liquid chlorine, or liquid chlorine and ammonia (chloramination) will stop the algae growth on the cooling surface.* Chloramination, *i.e.*, chlorination after adding ammonia to the water, causes chlorine to react with ammonia to form mono- or dichloramine according to the pH value. The chloramine is more effective and stable than chlorine alone, although the action is slower.

Sometimes without going through a formal treatment, formation of scale may be avoided by adding to the water a small amount of sodium metaphosphate or sodium pyro-phosphate. The phosphate seems to prevent effectively formation of the scale or incrustation, although the quantity added is far short in proportion to the amount of calcium and magnesium present. A case may be cited where cooling water containing 12-15 gr. of hardness (mostly temporary) as $Ca(HCO_3)_2$ which formed a bad scale in the cooling pipes, was successfully corrected by adding to the water only 5 ppm of sodium metaphosphate. The role the phosphate plays is therefore interesting.

More remarkable is the effect of the so-called "hexametaphosphate" on the behavior of calcium and magnesium bicarbonates in the water (temporary hardness). The "hexametaphosphate" seems to act as a deflocculant or peptizing agent to prevent deposition of calcium carbonate and magnesium carbonate precipitate. A very small quantity is sufficient to withhold precipitation of $CaCO_3$ and $MgCO_3$. Coagulation comes only after the water so treated has been heated, or after long standing. The addition to the water of such a small quantity of "hexametaphosphate" brings about a metastable state of supersaturation of the calcium and magnesium carbonates in the water, and is known as a "threshold treatment" for the water.† It appears that the function of the "hexametaphosphate" is to bring about a condition of supersaturation and inhibit the deposition of calcium and magnesium carbonate precipitate by adsorption on their nuclei of "hexametaphosphate," which thus prevents their growth beyond colloidal dimensions. For example, "hexametaphosphate," when added in a quantity of only 2 ppm to water containing temporary hardness as high as 600 ppm of $Ca(HCO_3)_2$, withholds separation of calcium carbonate until the water is heated to below the boiling point.

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* Nason, H. K., "Chemical Methods in Slime and Algae Control," *J.A.W.W.A.,* **30,** 449 (1938).

† Hatch, G. B., and Rice, O., "Surface-active Properties of Hexametaphosphate," *Ind. Eng. Chem.,* **31,** 51 (1939).

Hence this treatment is very useful for water which has a tendency to form hard scale on cooling tubes or in cooling pipe lines for multi-tubular coolers, condensers or heat exchangers in an ammonia soda plant, where water is the cooling medium. It appears, however, that the effect of "hexametaphosphate" is more on the calcium carbonate or magnesium carbonate, and not so much on magnesium hydroxide. Further, the use of hexametaphosphate-treated water tends also to loosen and re-dissolve gradually the scale already formed in the pipes. The "hexametaphosphate" seems to be adsorbed on the surface of steel, copper or brass, so that its effect is carried over. Therefore, by virtue of the hysteresis in its effect, this action persists even after the addition of the "hexametaphosphate" has been temporarily discontinued, so that the result is effectively and uniformly maintained, unaffected by any momentary fluctuations in the amounts of "hexametaphosphate" fed to the water. These properties have made "hexametaphosphate" a valuable reagent for the treatment of the scale-forming cooling water in an alkali plant, where the temperature of the exit cooling water seldom exceeds 80° C. This sesquestration of calcium and magnesium and other polyvalent ions from cooling water (though more or less temporary) is sufficient to free the cooling water system from scale formation and is very economical in its application because the quantity of the "hexametaphosphate" needed is so small. But because of the metastable and temporary character, this treatment would not be suitable for the treatment of hard water for boiler feed, except of course only for the prevention of the scale formation in pipe lines leading to the boilers.

Beneficial effects have also been obtained from the use of "hexametaphosphate" in the prevention of the formation of "mud balls" or in the removal of crust deposits on sand filters, and in the prevention of after-precipitation in the pipe line after the lime-soda treatment.

Chapter XXIV

Special Requirements of Ammonia Soda Industry

The ammonia soda process has been perfected by methods of gradual evolution. It has been developed by the highest skill and keenest observation. The pioneers in the industry incurred great expenses in working out the different steps by the introduction of many special features in the arrangement and construction of the apparatus to accomplish certain purposes. Experiments have been costly and experience has been painfully gained. Such little details as the U-loop seal, gas venting, overflow loop provision, orifice restriction, gas-lift effect, syphon effect, liquor suspension, gas locking, etc., are of the utmost importance in dealing with liquor and gas spaces in the practical arrangement of the apparatus, especially in a closed system under partial vacuum. Plants have undergone many changes as the operating conditions and the principles underlying each step of the operation have become better understood. Very few of the present ammonia soda plants remain as they were originally designed. These changes give some idea of the improvements that have been constantly effected in ammonia soda plants, though little information has become public. The difficulty of operation can be appreciated by realizing the single fact that the process tolerates no interruption, whether caused by the stoppage of the continuous flow of liquors or gas, or by the breaking down of any unit of the machinery. Although there is always a spare unit for every important unit of the equipment in the plant, absolute continuity of operation is not secured without the greatest effort. Even the liquor and gas piping sections must be carried in duplicate to enable one branch to be cleaned while the other branch is being used to carry on the process.

The rate of operation must be kept as uniform as possible. It is almost impossible to provide sufficient storage capacity for either the strong liquor, the filter liquor, or the crude bicarbonate, to tide over any length of period of stoppage in any one of the several divisions. Such matters, after all, can be provided only to a limited extent. Much has to depend upon continuous operation, drawing from the discharge of one unit and feeding into the next, and so on. Any trouble in the operation of one division is bound to be felt by the other divisions, and its effect in most cases is cumulative.

A study of the historical development of the ammonia soda industry shows that there were two stages in the operation of a plant. The first stage was to maintain the operation of the plant without interruption, so that a steady operation from the plant day after day for 365 days in the year resulted. In the second stage an effort was made to run the plant on

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the most economical basis, getting the maximum efficiency and capacity possible out of each piece of apparatus and reducing the losses and waste of raw materials to a minimum. Then, and only then, could an ammonia soda plant be said to have been placed on a firm foundation. Most of the work of modifying and altering the plant output as mentioned above took place during the first stage.

The material used for the construction of the apparatus is limited. The presence of ammonia in the gases and liquors unfortunately has eliminated the use of any copper, brass or bronze materials, which can be very easily worked and which have sufficient tensile strength for most purposes. They form, furthermore, valuable materials in combination with steel or cast iron in general commercial design. For copper and copper alloys are as a rule readily attacked by ammonia, showing a deep blue coloration.

Steel and wrought iron, although they have excellent tensile strength, lead very short lives in contact with ammonia gases or brine liquors containing ammonia and carbon dioxide, especially at an elevated temperature. The life of a steel tube in contact with hot ammonia and carbon dioxide gases or with hot ammoniated brine is from six months to a year, and that with cold ammoniated brine is from one to two years. Much trouble has been caused by the failure of cooling tubes made of standard boiler steel tubing. Only cast iron will satisfactorily withstand the corrosion. Unmachined cast-iron surfaces having a hard crust stand the corrosion better than machined faces. Special grades of cast iron, *e.g.*, "Meehanite," can be prepared which withstand corrosion better than the ordinary grades. It is imperative that only cast iron construction be used, wherever possible; an all-iron construction is a familiar specification for ammonia soda equipment.

Lead has excellent corrosion-resisting properties, but its softness limits its use to such matters as bell and spigot joint calking, gaskets for unmachined faces, cast iron tubing expanding, and some low-pressure work.

Corrosiron or Duriron (especially Durichlor) is resistant to the action of ammoniated brine or ammonium chloride liquors, but is very brittle and not machinable. It can be ground only, and is used in a limited number of places where the metal is not subject to mechanical or thermal strain.

High-chrome steels or chrome-nickel Stainless steels resist corrosion eminently well, although toward hot ammoniated brine, they are not so good as the high-silicon iron (Durichlor). The Stainless steels, such as 18-8 (meaning 18 per cent Cr and 8 per cent Ni on the average), 19-9, and scores of similar kinds under various trade names, are resistant to many chemicals. Among these, Type 304, containing low carbon, (.05-.06 per cent) are especially recommended, although special grades such as KA$_2$SMo, containing also 3-4 per cent Mo (Type 317), are more corrosion-resistant and cost considerably more. It is essential that these Stainless steels be heat-treated ("annealed") after all heating operations, such as electric welding, forging, touching with a torch, excessive cold working, etc., in order to restore their austenitic state. For only in the austenitic

state does the alloy develop its best corrosion-resistant properties, any crystallization in its grain structure or any segregation of carbon in the grain boundaries inviting attack by the action of chemicals. The so-called low carbon Stainless steels may not have carbon content low enough to be used without annealing after welding. Only the stabilized Stainless steels (such as Type 347 Cb-stabilized and Type 321 Ti-stabilized) may be welded without subsequent heat treatment. It is advisable to avoid direct impact of ordinary steel heavy tools (such as sledge hammers) on the Stainless steel plate or sheets during fabrication. The heat treatment consists in heating the alloy to above its critical temperature (generally from 1850 to 2050° F.) and then quickly quenching it in water (water quenching) or cooling it rapidly in air (air cooling), in order to preserve its austenitic state and allow no chance for crystals to separate. Whenever practicable, it is always recommended to "anneal" a
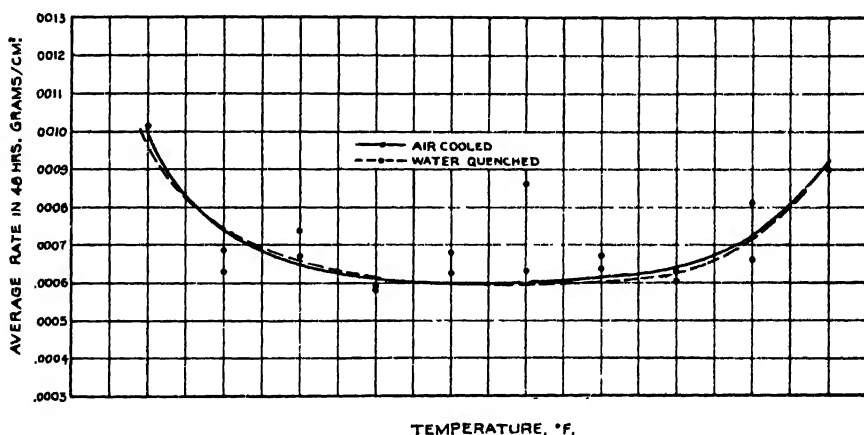
Fig. 114. Huey tests on type 304 steel tube. Average rate of penetration in 48 hours over a period of 240 hours.

Stainless steel piece after its complete fabrication and before it leaves the shop. With extremely low carbon content, however, such as in Type 304, annealing may be omitted where such annealing is impracticable for mechanical reasons. These Stainless steels, while quite resistant to the action of nitric acid and fairly resistant to the action of cold, dilute sulfuric acid, are not resistant to hydrochloric acid or hot ammonium chloride liquors. For plain nitric acid, straight chrome steels containing 14-18 per cent Cr (Type 430) or higher, are serviceable and cost less than the 18-8, but these high-chrome steels are usually harder to work with, and are not to be welded. To improve machining properties, sometimes .02.04 per cent Se or S is added to these Stainless steels. For high-temperature work, high chrome-nickel Stainless steels such as 25-20 (Type 310) are generally required because of their high heat-resistant properties. For electric resistance and high temperature, a high chrome-nickel alloy, "Nichrome" (Cr 15, Ni 60. Fe 25), has proved serviceable.

To help maintain the austenitic state of a Stainless steel working in the range of 800-1400° F., a "stabilizer" such as Cb or Ti is often added in small quantities (Cb 10 times carbon and Ti at least 4 times carbon). (See Types 347 and 321.)

Table 143 gives the composition of some of the commoner grades of Stainless steels, and Fig. 114 shows the relative effect of annealing a typical Stainless steel (Type 304) at different temperatures on the corrosion resistance, as determined by the Huey Test.

TABLE 143. Composition of Some of Commoner Stainless Steels.*

Type No.	Carbon	Chrome	Nickel	Other Elements
301	.09-.20	16.00-18.00	7.00- 9.00	Mn. 1.25 max.
302	Over .08-.20	18.00-20.00	8.00-10.00	Mn. 1.25 max.
302B	Over .08	18.00-20.00	8.00-10.00	Si 2.00-3.00 Mn. 1.25 max.
303	.20 max.	18.00-20.00	8.00-10.00'	S or Se .07 min. or Mo .60 max.
304	.08 "	18.00-20.00	8.00-10.00	Mn. 2.00 max.
308	.08 "	19.00-22.00	10.00-12.00	Mn. 2.00 max.
309	.20 "	22.00-26.00	12.00-14.00	
309S	.08 "	22.00-26.00	12.00-14.00	
310	.25 "	24.00-26.00	19.00-21.00	
311	.25 "	19.00-21.00	24.00-26.00	
312	.25 "	27.00-31.00	8.00-10.00	
315	.15 "	17.00-19.00	7.00- 9.50	Cu 1.00-1.50 Mo 1.00-1.50
316	.10 "	16.00-18.00	14.00 max.	Mo 2.00-3.00
317	.10 "	18.00-20.00	14.00 max.	Mo. 3.00-4.00
321	.10 "	17.00-20.00	7.00-10.00	Ti min. 4×C
325	.25 "	7.00-10.00	19.00-23.00	Cu 1.00-1.50
327	.25 "	25.00-30.00	3.00- 5.00	
329	.10 "	25.00-30.00	3.00- 5.00	Mo 1.00-1.50
330	.25 "	14.00-16.00	33.00-36.00	
347	.10 "	17.00-20.00	8.00-12.00	Cb 10×C
403	.15 "	11.50-13.00		Turbine quality
405	.08 "	11.50-13.50		Al .10-.20
406	.15 "	12.00-14.00		Al 3.50-4.50
410	.15 "	10.00-14.00		
414	.15 "	10.00-14.00	2.00 max.	
416	.15 "	12.00-14.00		S or Se .07 min. or Mo .60 max.
418	.15 "	12.00-14.00		W 2.50-3.50
420	Over .15	12.00-14.00		
420F	Over .15	12.00-14.00		S or Se .07 min. or Mo .60 max.
430	.12 max.	14.00-18.00		
430F	.12 "	14.00-18.00		S or Se .07 min. or Mo .60 max.
431	.15 "	14.00-18.00	2.00 max.	
438	.12 "	16.00-18.00		W 2.50-3.50
439	.50-.65	8.00		W 8.00
440	Over .12	14.00-18.00		
440F	Over .12	14.00-18.00		S or Se .07 min. or Mo .60 max.
441	Over .15	14.00-18.00	2.00 max.	
442	.35 max.	18.00-23.00		
442	.35 "	18.00-23.00		Cu 1.00
446	.35 "	23.00-30.00		
501	Over .10	4.00- 6.00		
502	.10 max.	4.00- 6.00 -		

* Courtesy, The Carpenter Steel Company.

In using Stainless steel in combination with other metals immersed in a chemical liquor, it should be borne in mind that generally speaking a Stainless steel behaves as a more electro-negative metal (is corroded faster) than silver, copper, brass, lead, nickel, or graphite, and as a more electro-positive metal (is less attacked) than ordinary iron, steel, aluminum, zinc, or cadmium, when local battery action sets in. In the ammonia soda industry, Stainless steel is commonly specified for the construction of the CO_2 compressor valves, valve seats, piston rods, etc. and for the construction of centrifugal pump rods, steam turbine blades, etc.

In all hot-working operations dealing with Stainless steels at a certain range of temperatures, care must be taken to look out for grain growth, air hardening, intergranular corrosion, cold brittleness, and other metallographical changes due to temperature effect.

For hydrochloric acid or strong ammonium chloride liquors, Hastelloy B, among nickel-molybdenum alloys, has stood corrosion well. Illium alloys are resistant to the action of hot ammoniated brine or hot ammonium chloride liquors. They are resistant to all chemicals (acids and alkalis alike) with the exception of hot hydrochloric acid or substances tending to liberate chlorine, such as $FeCl_3$. These alloys are machinable and are suitable for the construction of small parts, such as valves for strong liquor lines, although their cost limits their use.

Recently tantalum metal has been produced in quantities sufficiently large for commercial application. It is very inert metal like platinum and is not attacked even by aqua regia, chlorine, or chlorine products. It is an industrially valuable metal, combining mechanical strength and chemical resistance. Like tungsten, it has also a high melting point. It must, however, be treated as a semi-precious metal and its cost is far too high for general applications. It would be useful for making lining and clad vessels that resist corrosion of all chemicals except hydrofluoric acid and molten caustic soda (or hot strong caustic).

It is unfortunately true that solutions of chlorides, such as brine and ammonium chloride, that are met with in the alkali industry, are generally more corrosive than solutions of the corresponding sulfates and nitrates.

Aluminum is slowly attacked by strong ammoniated brine and its use is confined only to plain brine or weak sodium carbonate solutions.

Even cast iron is attacked by hot ammoniated brine or hot gases containing ammonia, carbon dioxide, and steam, but its corrosion-rate is slower than that of steel. Actually there is no metal or alloy of metals that is absolutely unattacked by this combination of materials at elevated temperatures; it is only a matter of the relative lengths of life and the cost of the materials that determine their fitness. Except in the gas system, where, if there are any valves at all, globe valves with hard rubber seating rings are used, the entire liquor system is equipped with cast iron cocks, ground metal-to-metal or packed inside with vulcanized asbestos packing. Lubricated cocks are very serviceable. They give tight service against corrosive liquors and their plugs are easier to turn. Sev-

eral makes, such as the "Merco Nordstrom," "Barco," etc., are available, but the ammonia soda manufacturers usually make them themselves. The industry is unique in that cocks instead of valves are extensively used throughout the plant. For simple hand operation, cocks are made up to 6 inches in size. From 8 inches up, such cocks require worm gear mounting for their operation. To enable all cocks to be opened or closed easily, whenever desired, their plugs are turned and lubricated regularly once a day. There is a special man in each division whose duty it is to look after these cocks and valves.

Nickel tubes and indeed all-nickel construction have been used in the construction of caustic evaporators and tanks for the manufacture of rayon-quality caustic.

A long list of different ferrous and non-ferrous alloys containing various percentages of chromium, nickel, molybdenum, cobalt, silicon, etc. that have been placed on the market under various trade names, could be given; but as their use in the ammonia soda industry is greatly restricted by their cost, such a list would have only an academic value.

A very complete catalog covering corrosion-resistant properties of metals and their alloys with their compositions as far as known, is pub-

TABLE 144. Metals Suitable for Different Liquors.

Liquor	Excellent	Fair	Unsuitable
Strong brine and calcium chloride solutions	(1) Lead (2) Nickel (3) Monel (cast)	(1) Cast iron (2) Copper (3) Aluminum (4) Steel	
Sodium carbonate solutions	(1) Chrome-nickel Stainless steels (2) Nickel (3) Monel (cast) (4) Illium	(1) Cast iron (2) Steel (3) Copper (4) Aluminum	
Caustic liquors (strong or weak)	(1) Chrome-nickel-molybdenum Stainless steels (2) Nickel (3) Monel (cast) (4) Illium	(1) Cast iron (2) Cast steel (3) Copper (4) Steel (low pressure work only)	
Molten caustic and fused calcium chloride	(1) Nickel	(1) Dense gray cast iron (2) Nickel cast iron	
Ammoniated brine	(1) Chrome-nickel-molybdenum Stainless steels (2) Lead (3) Illium (4) Nickel	(1) Cast iron	(1) Copper, brass and bronze (2) Wrought iron and steel tubes (3) Aluminum
Mother liquor and filter liquor	(1) Chrome-nickel-molybdenum Stainless steels (2) Lead (3) Monel (cast) (4) Nickel (5) Illium	(1) Cast iron	(1) Copper, brass and bronze (2) Wrought iron and steel tubes

lished by *Chemical and Metallurgical Engineering,* entitled "Data Sheets on Materials of Construction."

Table 144 gives some suggestions concerning materials to be employed for parts in contact with different liquors in the soda industry. "Excellent" means "rather durable"; "fair" means "commercially applicable"; and "unsuitable" means "chemically attacked."

The contents of Table 144 can be compared with an article by Mr. J. L. Everhart, entitled "Materials That Resist Alkali Corrosions." *

From Table 144 it will be seen that a good grade of cast iron or nickel cast iron is by far the most commonly used material. It is used because of its good resisting quality and its cheapness. For caustic liquors at high temperatures and pressures, steel vessels and wrought-iron tubes are subject to caustic embrittlement. For ammoniated brine which contains

Fig. 115.

Slip blank.
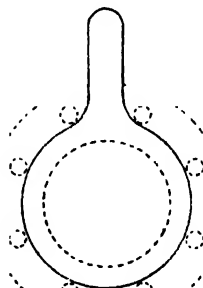
magnesium salts that form scale or coating on the internal walls, steel vessels and steel pipes are protected against corrosion by the coating formed. Often a metal surface that has been completely submerged in the liquor is less attacked than the portion in the gas space or partially exposed to the air, *i.e.,* at the junction between the liquor and gas phases.

Impellers of centrifugal pumps made of cast iron are frequently pitted or eaten up by the hot ammoniated brine or hot filter liquor. So also are the cast-iron cocks. As a rule, the cocks for this service will leak and will not hold the liquor if proper maintenance is not effected. When no leakage may be tolerated, as is the case when one portion of piping is taken down for cleaning or for a change-over, a "slip blank" must be used. This slip blank is made of $\frac{1}{16}$-inch or $\frac{3}{32}$-inch steel plate cut with the diameter, which just fits the inside circle of the bolt holes in the flange. It is inserted between the flange joints with a rubber gasket on each side. These slip blanks are provided with handles (Fig. 115) and are very useful for the gas system as well as for the liquor system. Sometimes no valves are provided at all, the cutting-out of one branch being done by means of these slip blanks. The change-over from one section of piping to another frequently involves removing these slip blanks from one set of

joints and inserting them in another. Piping systems of various sizes are usually flexible enough to enable the flange joints to be pried open with a flat chisel and these slip blanks to be inserted between the flange faces.

All over the plant, wherever liquids, such as raw brine, milk of lime, filter liquor, etc., are introduced into any apparatus, they are measured through orifice plates similar to the above slip blanks but with a round hole of the proper diameter in the center, regulating the flow by the head of the liquid above the orifice plate. The orifice diameter is to be marked on the handle. Where a constant rate of feed is desired, the constant orifice head is further regulated by means of a float control. Probably in no other industry is the regulation of rates of different liquor feeds carried out more systematically and with more minute precision than in the ammonia soda industry.

Ammoniated brine and other hot ammonia liquors are also very corrosive in their effect on the packing material and pipe joints. Drippings from packing glands and pipe joints are annoying and make the plant intolerable. Packings for centrifugal and plunger pumps must be of a lead-graphite-asbestos composition or of a very soft metallic packing. To avoid leaking, these stuffing boxes must be extra deep. Flange gaskets are cut from $\frac{1}{16}$- to $\frac{3}{32}$-inch pure rubber sheets.

Leakage is something that cannot be tolerated in ammonia soda plants not only from the viewpoint of keeping the apparatus and floors clean, but also of protecting the life of the equipment. Any leakage of liquor due to a slight ooze from the pipe flanges or threaded joints, or from the overflow cover, manhole cover, or tapped hole through the cast iron wall will soon cause the wetted metal surface, even of cast iron, to become corroded and gradually eaten through. It is not an unusual thing to see steel bolts in a leaky flange joint "frozen" in their holes or else rusted so badly that threads have been destroyed, because ammonia brine liquors are especially corrosive in contact with air. Leakages at the top flanges of cast-iron cocks, though a rather common sight, are subject to the same objection. All leaks should be stopped at the very beginning of their appearance: the white salt crystals appearing on the surface of the apparatus or hanging from pipe flanges should receive prompt attention from the men in charge. If these leaks are not stopped at their first appearance, they will be more difficult to remedy later. If cast-iron cocks leak at the packing glands or do not hold tight, the packing gland bolts should be immediately tightened. If such leakage is allowed to go on for several days, the contact surface of the plug will have been corroded by the liquor and the plug will no longer fit tightly, however firmly the bolts are tightened later. Cock plugs should always be kept down. Even if the gland bolts have to be loosened for turning the plug, they must be tightened back immediately after the plug has been turned to position.

As it is necessary for frequent change-overs to be effected very quickly, there will be occasions for opening up pipe flanges, manhole covers, etc. Since the atmosphere is very corrosive in the works, all bolts used in pipes, flanges, manhole covers, etc., must be of exact lengths flush with

the top of the nut. It should be a practice with the men in the plant never to use longer bolts with their threads projecting much beyond the nut. Inside the apparatus in contact with the liquor, nothing but through bolts preferably in cored slots is allowed, as stud bolts or cap screws in contact with liquor are unsuitable where opening or overhauling for cleaning is necessary.

The ammonia soda industry is also unique in that large volumes of liquids and gases are handled throughout the entire process. Fortunately, generally speaking, they are all under low pressures or partial vacuum, and it is interesting to note that wooden plugs frequently suffice to stop various holes provided for rodding, for observation, or for other purposes.

Because of various streams of fluid flow under low pressure or under partial vacuum, the plugging tendency of different passages must be constantly guarded against by the operators. This plugging may be caused by the mechanical deposition of solids carried in the liquor, by the formation of hard crust around the internal walls of liquor pipes, by the crystallization of ammonia compounds from ammonia and carbon dioxide gases at a low temperature, or by the chemical reaction of the constituents in solution upon the internal walls of the pipes. The difficulty arising from this cause will not be fully appreciated by those unfamiliar with the process. Although it is impossible to enumerate all points where plugging is likely to occur, several salient places can be mentioned here. In the kiln gas scrubber, the gas down-take at the entrance to the scrubber is likely to be choked by dust collected from the kiln gases. In the distiller condensers, the furnace condensers, and other gas coolers for ammonia and carbon dioxide, the gas passages may be choked by the deposition of ammonium carbonate and ammonium carbamate crystals when the temperature is reduced below a certain point. In the liquor system of the ammonia absorber and settling vats, the overflow passages and piping connections tend to become plugged by the soft "mud" accumulated in these places and by the hard scale formed in contact with the ammoniated brine. The presence of "mud" in the liquor, coupled with the fact that the flow is under a partial vacuum, makes the flow of the brine very sluggish and the "suspension" of liquor due to gas locking and mud restriction is likely to occur in the absorber system, if such matters as gas venting, inclined gravity flow, freedom from downward loop (mud trapping), freedom from upward loop (gas pocketing), etc., have not been carefully observed.

It may be remarked that, in general, a simple and direct piping should be arranged for the liquor flow; that these liquor pipes should be inclined wherever possible toward the direction of the flow to avoid any upward or horizontal sections where "mud" may be accumulated, and to aid the venting of gases out of the liquor stream toward a higher point; that the ammoniated brine pipes should have ample cross section for the brine to flow, allowing for the constriction by scale formation; that the overflow openings should be sufficiently wide to provide ample width for the liquor and the "mud" to flow; and that all overflow shoulders or horizontal edges should be as short as possible. Even in the piping system which contains

clarified ammoniated brine, the flow may often be restricted by the for-
mation of hard scale in the pipes.

That this apparently clear ammoniated brine gives rise to scale forma-
tion in the pipes is proved by the fact that an 8-inch strong liquor pipe
left only a 4-inch opening after having been in use for about 6 or 8
months. This scale consists mostly of magnesium carbonate, for it is
very difficult for magnesium mud to settle completely and traces may
remain in colloidal suspension in the "settled" ammoniated brine. The
mother liquor or filter liquor, however, is not so likely to form scales in
the cocks and pipes as ammoniated brine (or strong liquor) and it is also
not so corrosive. In the distiller, the heavy liquor in the lime still tends
to deposit solids on the division plates, under the "mushrooms," and at
the overflow edges and overflow trough bottoms, causing plugging. In
the course of time a hard scale will be formed as thick as 2 to 3 inches.
The period of cleaning may vary from a couple of weeks to a couple of
months depending upon the character of the lime and upon the manner of
operation. In the blow-off line, where the distiller waste (or run-off-
liquor) is sent out by the natural distiller pressure without the aid of a
booster pump, the discharge may become very sluggish because of restric-
tion in the pipe lines by the formation of hard scale or by the deposition
of solids. In the furnace gas main at the uptake, the soda dust that is
carried in the gas frequently collects in the main and chokes the gas
passage. Provision for a water pipe for flushing with water and an open-
ing for rodding the pipe is quite necessary. In the carbonating towers,
solid sodium bicarbonate coating formed on the cooling tubes and mush-
rooms may choke the gas and liquor passages. The difficulty is overcome
normally by the so-called "cleaning" with green liquor at a compara-
tively high temperature every 4 or 5 days. If the green liquor carries any
suspended magnesium mud, magnesium carbonate will be deposited in the
columns, especially at the upper part, forming a solid scale that cannot
be taken care of by the ordinary method of cleaning, and the columns will
eventually be put out of commission. If, for any reason and for any
length of time, the carbon dioxide gas from the compressors delivered to
the towers is interrupted, a complete settling and plugging of the column
by the bicarbonate certainly results. This is one of the most serious cases
of plugging that can occur in any apparatus. When such an accident
happens nothing but shutting down the tower in question and cooking the
content with water by means of steam can remedy the trouble. This does
not or should not usually happen. This cooking may cause leaks in tube
sheets or in cooling box covers, and will result in a low-grade and off-
color ash when the column is started again. In ordinary cases, however,
shooting in steam through the draw opening and around the sides of the
bottom ring for a few minutes suffices to open up the column.

In the suction and delivery lines of the lime pump handling milk of
lime for the distiller and of the mud pump pumping mud from the settling
vats—for both of these services only a plunger-type pump fitted with ball
valves is satisfactory—unless the work is attended with intelligence and

care, plugging of the pipes by solids settled therein is a source of trouble and delay. Provisions in such lines for flushing with water, rodding out the solids, and cleaning the sections concerned, are made by means of tees
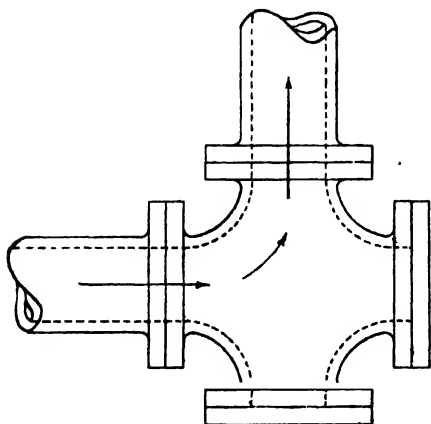
Fig. 116. Cross in place of horizontal elbow.
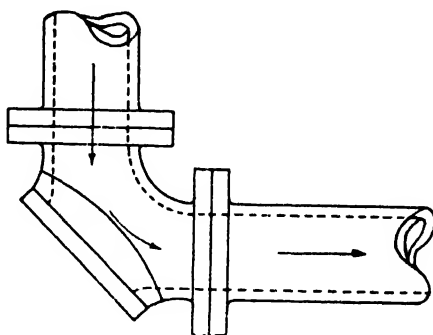
Fig. 117. Elbow with specia opening.

and crosses with blind flanges. In the centrifugal pumps for ammoniated liquors—which are most extensively used for pumping liquors in the works—the impeller ports are frequently restricted or even plugged by a hard scale formation and then the pump fails to deliver the quantity of liquor required. Unlike the pumps for filtered liquors, these strong liquor pumps have a very severe duty. To give an extreme case where plugging is least expected, it has been the writer's actual experience that the 8-inch
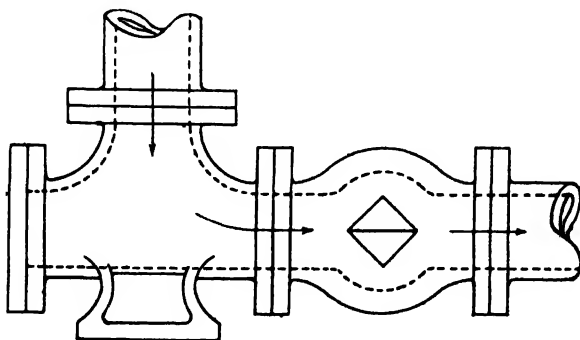
Fig. 118. Tee in place of vertical elbow.

vacuum main at the gas outlet from an ammonia washer using fresh brine was plugged by the gradual deposition of solid sodium chloride entrained in the gas bubbling out of the top compartment over a tall gooseneck.

It is good practice to use crosses and tees in such pipe lines provided with blind flanges so that, when cleaning is necessary, these blind flanges can be opened (Figs. 116, 117, 118, and 119). The cocks are set next to the crosses or tees (Fig. 118) to enable them to be rodded in case of plugging
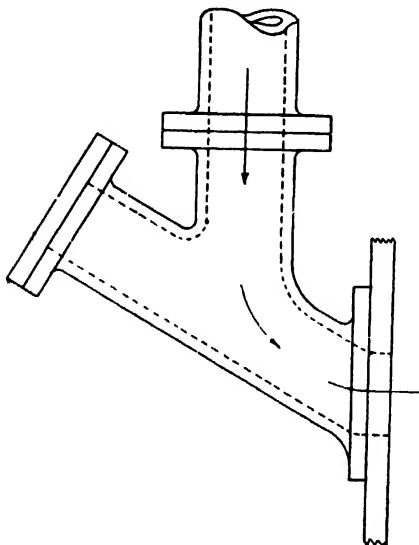
FIG. 119.
Special inlet nozzle.

or restriction in the opening. Often, a hand pusher (Fig. 120) is provided at the end of a pipe or opposite an opening to scrape off scale in the opening of a cock or of an overflow.

In the cases of gases containing ammonia and carbon dioxide there is always danger of crystallization when the temperature gets too low for any length of time. This is due to the formation of solids which consist of carbonates and carbamate of ammonia. The composition of these crys-
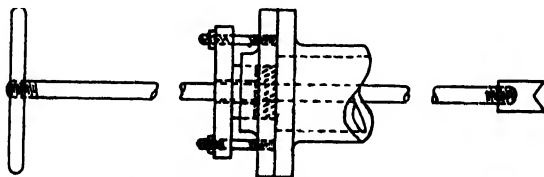
FIG. 120. Scale pusher for cock opening.

tals and the critical crystallization temperature depend upon the composition of the gas and the relative concentration of ammonia and carbon dioxide in it. At the tail end of the absorber system where the gas has been more or less scrubbed by brine, crystals are sometimes formed in the main when the temperature gets very low, and these crystals are found to have the composition given in Table 145.

TABLE 145. Composition of Crystals Deposited at Tail End of
Absorber System.

	Per Cent
Ammonium carbonate, $(NH_4)_2CO_3$	47.61
Ammonium carbamate, $NH_4 . NH_2CO_2$	42.23
Ammonium bicarbonate, NH_4HCO_3	8.80
Ammonium chloride, NH_4Cl	1.34

In the distiller condensers where the gas is rich in ammonia but not so rich in carbon dioxide, the critical crystallization temperature is generally around 55° C., as has been mentioned in connection with the absorber operation (see Chapter VII).

In the case of furnace condensers, however, since the gas is richer in carbon dioxide than in ammonia, the crystals formed at a low temperature consist almost entirely of ammonium bicarbonate. The analysis of crystals deposited in the furnace gas main is given in Table 146.

TABLE 146. Composition of Crystals in Furnace Gas Main.

	Per Cent
Free ammonia NH_3	20.81
Total CO_2	53.57
Total Cl_2	Trace
Fixed ammonia (NH_4^+)	Nil

Thus these crystals contain 96.70 per cent NH_4HCO_3.

In the event of plugging or constriction of the gas passage in a cooler or condenser due to crystallization of solids when the temperature for some reason falls too low, a sure remedy is to introduce some exhaust steam to warm up the apparatus, thus decomposing the solids and opening the passage.

In the operation of ammonia soda plants there are the so-called cycles. The well-known ones are the ammonia cycle and the carbon dioxide cycle. Ammonia gas is generated in the distiller, absorbed by brine in the absorber, passed in the form of ammoniated brine through the carbonating towers, drawn out in the form of mother liquor with ⅔ to ¾ of the free ammonia converted to fixed ammonia, and finally sent back as filter liquor to the distillers for the regeneration of ammonia. This is the ammonia cycle. As for carbon dioxide, half of the carbon dioxide in the bicarbonate drawn from the tower is recovered from calcination in the soda dryers and returned to the towers either separately or mixed with the kiln gas. This is one branch of the carbon dioxide cycle. Another branch is represented by carbon dioxide dissolved in the mother liquor as ammonium carbonate, sent to the distiller in the form of filter liquor, recovered with ammonia from the distiller, absorbed by brine in the absorber as ammonium carbonate, and sent back to the towers in the form of the partially carbonated ammoniated brine (containing 45 to 55 grams of carbon dioxide per liter). That part of the carbon dioxide existing in the gaseous phase in the absorber system under partial vacuum is pumped through the exhauster as spent gases containing as high as 60 to 70 per cent carbon

dioxide by volume (the balance air) and is sent back to the columns with the dryer gas through the carbon dioxide compressor intake.

Then again there is the balancing of operations in the different divisions of the works. If the operation in different houses is not properly balanced, the whole plant cannot operate to the fullest capacity, and also high operating efficiency or economy cannot be secured. A balance of operations exists in each of the following divisions:

(1) **Between the Tower House and the Dryer Room.** The rate of furnace operation must keep step with tower operation. A changed condition in the furnace operation causes a change in the tower operating conditions. If furnace operation is interrupted for any reason, the volume of the dryer gas is diminished or the concentration of the gas is decreased, the decomposition and the output from the towers are correspondingly decreased, and further the crystalline character of the precipitated bicarbonate is altered. This means that less bicarbonate is produced to feed the dryers and also that poorer bicarbonate crystals are formed for the dryers. The result is a still poorer gas returned from the dryers to the columns. Thus, the cause and the effect are interrelated and persist in a cycle only to become worse as the cycle is repeated. The solution lies in keeping a certain quantity of bicarbonate on the floor to meet these emergency conditions. An attempt should, of course, be made to avoid any occurrence of such conditions.

(2) **Between the Tower House and the Distiller House.** The rate of distillation must keep step with the tower operation. If the towers are drawn faster, more ammoniated brine is required, and more filter liquor is produced; then the distillation operations must necessarily be speeded up to take care of the increased volume of the filter liquor and to meet the increased demand for ammoniated brine. If the filter liquor is not sufficient to maintain the distiller operation for the production of the ammoniated brine required, then crude liquor or ammonium sulfate solution must be added to replenish the deficiency of ammonia in the system. The two houses must be kept in balance and the best policy is to secure absolute uniformity in the rate of operation on each side.

(3) **Between the Engine Room and the Distiller House.** The power consumption in the engine room must be so adjusted that the exhaust steam produced is just sufficient for distillation purposes. A higher power consumption, and consequently steam consumption, not only puts an extra load on the boilers and increases the coal bill, but causes a surplus of exhaust steam over what can be used in the distillers. This excess steam may have to be let out to the air. It represents a waste of coal, unless it can be condensed back as in the bleeder turbine arrangement. This problem has been discussed in the chapter on "Generation of Power for Ammonia Soda Plants," and the reader is referred to that chapter.

(4) **Between the Lime Kilns and the Distiller and Tower Houses.** The production of lime in the kiln for the distiller operation and of CO_2 gases for the column operation must be so adjusted that the rate of operation in this triangular relationship may be kept in good harmony. Usually

there is an excess of the kiln gas to be allowed to escape into the atmosphere. The determining factor is the rate of lime consumption in the distillers. Where there are simultaneous demands for lime for caustic soda manufacture and for kiln gas for refined sodium bicarbonate manufacture, the operation of the lime kiln then may not be under exclusive control of the distiller operation.

Consideration of the various phases shows that an absolutely uniform and constant rate of operation in each and every division of the works is a *sine qua non* for ease of control, for regularity of output, and for high efficiency and economy in manufacture.

To maintain continuous operation and to provide for failure in power transmission and lighting lines, it is generally recommended to have more than one feeder circuit over which power may be obtained. Since several of the drives in an ammonia soda plant require the utmost continuity of service, a number of ways are adopted for obtaining it. A failure of power in the electric motors at the rotary calciners (for instance) might cause an extremely expensive shut-down due to the high temperature at which these shells are operated. Occasionally a gasoline engine is installed and serviced for continual stand-by so that the shells of rotary dryers can be operated almost immediately, should all sources of electric power supply fail. A source of purchased electricity available for stand-by or break-down service is often justified. Generally, however, to avoid damage to the dryer, hand-operated mechanism is provided (in case of emergency) for such purposes.

As the operation in the ammonia soda plant is strictly continuous and any accidental loss due to personal inattention on the part of the operators may run to large figures, it is always a good policy to provide recording and integrating meters at various points in the process. Such installations will soon pay for themselves. These include recording thermometers or pyrometers, recording pressure or vacuum gauges, recording flow meters for steam and water, recording CO_2 meters in the flue gases, and such other recorders as the Esterline-Angus recorder for ammonia at the bottom of the ammonia distiller, etc. The electrically operated type is often to be preferred.

As in all industrial plants, an iron cement, of which many commercial brands are available, is very useful and handy in making repairs due to cracking or corrosion in cast iron or steel body, and in making tight joints that do not have to be taken apart in the future.

Consideration of special requirements will not be complete without a discussion of surface protection for materials of construction in an ammonia soda plant. The paint materials generally have the following bases:

(1) Oxidizing vegetable oils (linseed oil base)
(2) Phenol formaldehyde resinoid (Bakelite base)
(3) Asphaltic material
(4) Chlorinated rubber

and contain the following principal pigments:

(1) Iron oxide
(2) Basic lead oxide
(3) Titanium oxide
(4) Aluminum and aluminum alloy metal powders
(5) Graphite

A strong alkali is the active ingredient of one important class of "paint removers." It is therefore to be expected that the surface protection problem in an alkali plant is difficult and not entirely solved.

The service in the ammonia soda plant can best be discussed under separate headings of "dry" and "wet." The dry side includes the interiors of those divisions for calcining the crude bicarbonate, etc., and all other places where there are seldom occasions for steamy conditions or condensations of vapor to form alkali solutions on the wall surface. The wet side covers those divisions dealing with ammoniated brine, and CO_2 and ammonia fumes, and has either frequent condensations or occasional spillages and sprays of alkaline or ammoniacal liquors. In both services, the air contains alkali dusts, CO_2 gas and ammoniacal fumes.

Reinforced concrete columns and beams deteriorate in the presence of these fumes, if the concreting job was not done properly and the concrete mass is porous. The steel bars inside the reinforced concrete columns and beams have been known to corrode under these circumstances.

On structural steel around a high ambient temperature and near gas vent from an apparatus which operates at a temperature of 60 to 90° C., a reasonably good and moderately permanent protection against alkali dust and brine spray is obtained by spraying the surface with heavy fuel oil containing a measure of rosin oil and Portland cement. This is an especially inexpensive coating. On cooler surfaces it remains objectionably sticky, whereas on the warmer surfaces it dries eventually to a sort of varnish-like surface.

In the dry parts of the plant, the linseed oil-lead pigment paints have an appreciably shorter life than the resinoid-titanium pigment paints, although the latter have a greater chalking tendency than the former. The resinoid-aluminum pigment paints have preferred applications on warmer surfaces (up to 250° C.). They also do reasonably well on surfaces occasionally subjected to ammoniacal fumes. The iron oxide paints in linseed oil have the shortest life of those listed. Where soda ash dust becomes damp and wet through humidity changes, the life of any paint is short. The most severe service is near the outlets of the brine-scrubbed carbonating tower.

It appears that in the crude bicarbonate and soda ash divisions the asphaltic base paints with essentially graphitic constituents have the longest life. Their black color, however, makes them undesirable in many locations and applications. One good grade is the so-called "Ebonol" made by Sherwin Williams Company, and is applied by means of a spray gun. The air pressure on the gun is 35 to 40 lbs. gauge and that used on the tank is 15 lbs. Fifty feet or more of a $\frac{7}{16}$-inch rubber hose is used

for the air line to the tank; and 25 feet of a $\frac{3}{16}$-inch hose are used for air and 25 feet of a $\frac{1}{4}$-inch hose for paint, from the tank to the spray gun. When a light color is desired, a thin coat of aluminum paint may be applied on the surface of "Ebonol."

In the caustic soda plant, corrosion is not as severe as in the soda plant. Unpainted structural steel rusts more slowly, although wood and timber may suffer severe deterioration. For resistance against the attack of caustic soda solutions in concentrations up to 50 or even 70 per cent, the rubber base paints have been found to be the most suitable. The Hercules Powder Company's chlorinated rubber paint, manufactured under one of the German patents and bearing the trade name "Tornesit," and the Goodyear series of "Pliolites" are in use. Lately, for same service, ethylcellulose has been patented by the Pittsburgh Plate Glass Company. These materials have been used for lining stationary tanks as well as tank-cars, and also for painting structural steel, such as columns, girders, beams, etc. In the caustic plant itself, neither linseed-oil base nor bakelite base paints with lead or titanium pigments have been found satisfactory because of the caustic atmosphere. The asphaltic paints do better and are cheaper.

In electrolytic and chlorine products plants, the corrosion is generally more severe than in others. The same generalities apply, but life of coatings will be found to be shorter. Chlorine attacks metal surfaces. Brick or concrete construction is preferable. In the caustic fusion room, no paint will resist attack by caustic fumes and last for any length of time.

In the electrolytic sodium chlorate plant, no wooden structure is tolerated because of the inflammable or explosive character of wood or any combustible matter when soaked and dried with sodium chlorate liquor. Men around the plant must wear rubber garments and rubber boots to avoid fire hazard caused by sodium chlorate.

The most logical attack on the alkali plant paint problem lies in the removal or mitigation of the source of trouble. Exhaust vent stacks can be relocated or extended. Overflow ducts, splash guards, etc., can be studied critically and provided for in order to eliminate causes of accidental spillage, formation of spray, sources of fumes, etc.

"Guniting" has been found very useful for protecting the surfaces with cement where a rather heavy coating is desired. For this purpose three bags of coarse sand are taken and mixed with one bag of cement, using three gallons of water. Sand for "Gunite" should not be mixed with cement more than an hour before application. The mixture must be of right consistency: if too wet, the coating would be thin and porous, and if too dry, it would develop cracks and voids. The nozzle of the gun should be held 3 or 4 feet from the surface and the air pressure should not be excessive. Two coats are generally applied, the first coating being about $\frac{1}{4}$ inch thick, while the second coating may be as much as $\frac{3}{4}$ inch thick. Workmen should be provided with goggles to protect their eyes and with respirators to guard against inhaling silica dust.

Chapter XXV

Control in Ammonia Soda Process

Chemical control in a process differs from chemical analysis in that, owing to lack of time, only such tests or analyses as can be rapidly and readily carried out by the operatives in the field are made and the results are awaited to guide the operation immediately. Less accurate but more rapid methods must often be adopted, and tests which are indications, though not strictly accurate, are used because of their convenience in execution. More accurate and' complete analyses are usually relegated to the chemical laboratory to be accomplished by regular analysts. The control tests should be made at least hourly and, where necessary, as for the excess lime at the distiller bottom, and for NH_3 and Cl^- titers in the absorber bottom, the tests are made at intervals of a few minutes. Unless explicitly mentioned, such tests are made hourly. Results, however, are always entered hourly in the works log sheets.

In addition to chemical tests it is essential to regulate the temperature and pressure (and vacuum) conditions in the apparatus and at various points in the system. Where orifice regulation is used, the diameter of the orifice and the head of the liquor above the orifice must be properly adjusted.

Brine department. It is first necessary to ascertain if the brine is saturated. Strictly speaking, we are interested in the concentration of sodium chloride or other sodium salts present in the brine, *i.e.*, of sodium only, but as no rapid method is available for the determination of sodium, the chlorine determination by Mohr's method is taken as representing sodium because of its rapidity. This is not accurate inasmuch as not all Na is present as NaCl and not all Cl is combined with Na. If the composition of brine runs approximately constant, however, a factor can be found to determine the concentration of Na from that of Cl found. Usually the specific gravity of the brine is taken. But if the brine contains many impurities, the specific gravity of the brine runs higher than that which corresponds to the amount of sodium chloride present. Saturated sea brine gives a specific gravity of 1.205 to 1.215 at 15° C., which is considerably higher than that of the pure saturated brine at this temperature. It is necessary to have the brine fully saturated. Its Cl^- titer should run 107 to 108.

When raw brine is to undergo chemical treatment before it is sent into the system, close control must be exercised as to the regularity and quantities of the reagents added. The temperature and the pH value of the brine during treatment must be carefully adjusted and recorded. The purging of the mud from the settling system, or mud pumping, should be

done regularly and scrupulously so that excessive quantities of brine may not be wasted.

Lime department.   In the lime kiln the kiln gas should be sampled at least hourly and tests for the percentage of carbon dioxide, oxygen and carbon monoxide made with an Orsat.   There should be practically no carbon monoxide, but there may be a small fraction of a cc. of oxygen. For efficient operation the temperatures of the kiln exit gas from the top and that of the lime drawn from the bottom should both be low.   Thermometers should be provided in the top gas down-take and in the lime draw.   The temperature of the exit gas should be around 80° C. and that of the lime 50° C.   The milk of lime going to the distiller should be kept hot (around 80° C.) and should be as concentrated as the pipe lines and pumps can handle it.   The strength of the milk of lime should be carefully watched.   Ten cc. should be pipetted and diluted to 100 cc. and 10 cc. taken for analysis by titrating with N HCl using phenolphthalein as an indicator.   The CaO titer should be around 180, which corresponds to about 250 grams CaO per liter.   Too weak (dilute) a milk of lime unnecessarily increases the volume of the liquor to be distilled and causes high consumption of steam for distillation and loss of ammonia in the distiller waste.   Unless the limestone is very poor and the lime improperly burned, such a strength of milk of lime (250 grams of CaO per liter) should not give much trouble.   When the limestone is of a very poor quality, such a high concentration of milk of lime may be difficult to handle without plugging up the pipe lines.   To ascertain the strength of the milk of lime the specific gravity can be taken with a hydrometer or, better, by weighing the milk of lime in a bottle of a 100 cc. volume and known tare.   The hot lime liquor of good strength should have a specific gravity of about 1.20.   Attention should be called to the fact that the specific gravity reading gives only a very rough indication of the strength of the milk of lime, as the reading is affected by the amount of solid impurities in the lime.   The pressure of the blast entering the bottom of the kiln is taken by a water manometer and the blast adjusted to the rate of operation.   For a kiln say 70-80 feet high, the blast varies from 4 to 8 inches of water, depending upon the rate of burning and the size of the stone charged.   A water manometer is provided in the gas outlet pipe to measure the pressure condition in the kiln top.   Where the kiln cover and casing are reasonably air-tight, the kiln should be operated under a very slight vacuum to aid the decomposition of limestone. Usually, however, for fear of leakage of air inward, a slight positive pressure instead of vacuum is employed.   The ratio of the stone to coke is important.   Both the stone and the coke in the charge should be weighed and recorded.   Too much coke gives a low gas test and causes overburning of lime, while too little coke yields excessive underburned lime, *i.e.*, lime with a stone core.   The different sizes of the stone are best sorted and burned separately.   The smaller size of stone takes less coke than the larger size and less time to burn.   The difference of a single pound of coke in a carload of charge (1 ton of stone) makes a noticeable difference in the

results of the kiln operation. Sizes from 6 to 2 inches, however, may be burned together. The proportioning of coke to stone may be done in a multiple hopper feedtable.

In the kiln gas main from the kiln down-take, through the scrubber and the cleaner, and finally all the way to the CO_2 compressor intake, at a half dozen or more points the line must be provided with U-tube manometers, each to indicate the pressure or suction conditions at the respective places. At the kiln end, the down-take and the inlet to the scrubber are likely to be plugged by the fine dust in the gas carried over from the kiln; while between the scrubber and cleaner outlet and the compresser intake, the pipe is sometimes flooded at low points by the condensate or water entrained in the gas from the scrubber and cleaner. This restriction to the gas passage causes a high vacuum ahead of the obstruction and affects the distribution ratio between the kiln gas on the one hand and the furnace gas on the other, when the compressor is to send mixed gases to the columns from the two sources. The manometer indications help locate the place of restriction. Generally normal vacuum (or pressure) readings are posted at the respective spots so that when the manometer reading at any particular spot exceeds the reading given, it indicates to the operators that the section beyond that spot needs cleaning or perhaps the condensate there needs more thorough draining. A systematic charting of the suction or pressure conditions throughout the whole system is worked out for the guidance of the operators so that internal obstruction at any point of the system can be readily spotted out and the necessary cleaning or draining applied immediately. All this should be attended to before the trouble begins to be felt in plant production.

Absorber and vat house. Tower washers and filter washers are placed under the charge of the absorber rather than the tower men, as the brine used for scrubbing is all to be sent to the absorber for final ammoniation. All brine inlets to this apparatus should have orifice and float regulations in order to adjust the rate of flow accurately. The head above the orifice plate for a given orifice diameter should be recorded. In these washers, the temperature at the bottom compartment should be taken as well as that of the fresh brine at the top inlet, as the absorption of ammonia by brine is largely dependent upon the temperature of the brine. Samples of brine from the top compartments of these washers should show no ammonia titer. All the scrubbing brine ultimately flows by gravity through the absorber washer to the absorber. From the bottom compartment of the absorber, samples of ammoniated brine should be taken every 5 minutes or oftener to determine the NH_3 and Cl^- titers. These two titrations can be profitably done in one sample by first titrating for free ammonia with N H_2SO_4, using methyl orange as the indicator and then adding a little calcium carbonate powder after diluting the solution, titrating by Mohr's method for chlorine with N $AgNO_3$, using potassium chromate as the indicator. The flow of brine to the absorber is adjusted according to the rate of distillation. The Cl^- titer must be maintained as high as possible but cannot be much above 260 grams of sodium chlo-

ride per liter. The NH_3 titer is maintained at a fixed ratio to the Cl^- (about **1.10:1**).

Thermometers should be provided at the absorber bottom compartment, in the liquor line entering the absorber cooler, in the liquor line returning from the absorber cooler, and finally at the gas outlet from the absorber top. These temperatures are important, as ammonia absorption is a function of temperature. When the body of the absorber is hot to the top, known as "hot top," because of either insufficient cooling surface in the absorber cooler, excessive steam carried over by too hot an ammonia gas to the absorber, or too little or too warm brine being used in the absorber, ammonia will not be readily absorbed in the liquor but will pass out from the top and may even be drawn finally to the vacuum pump. The temperature at the absorber system, therefore, is very important and a recording thermometer should be installed to show the condition of the absorber exit during the 24 hours. This top temperature of the absorber washer is normally 35 to 40° C. The absorber liquor outlet to the vats should be provided with a thermometer and this temperature is from 60 to 65° C., a temperature quite suitable to give good settling of the ammoniated brine in the vats. Through these settling vats, by atmospheric cooling, the temperature of the ammoniated brine is reduced somewhat, until at the inlet to the brine coolers or vat coolers it is about 50° C. The brine coolers (or vat coolers) should bring the temperature down to about 30° C. At these places thermometers are provided to observe the temperatures mentioned. The temperature of the cooling water at the inlet and at the outlet of these coolers should also be observed.

From the bottoms of the settling vats the mud should be pumped by a plunger type pump in rotation. The number of minutes for mud pumping for any particular vat to reduce the mud content therein to, say 25 per cent (by volume) should be noted. This establishes a time schedule for mud pumping. In the absorber system mercury manometers are provided to register the vacuum conditions at different points and to detect any gas-locking (liquor suspension) or plugging tendency in any part of the system. The following points in the vacuum system should be provided with manometers:—Absorber exhauster, top of absorber washer, top of absorber, outlet of distiller condenser, and top of distiller. These vacuum conditions vary as the depths of wash (barbotage) in the different parts of the apparatus. If the apparatus and pipe lines are clean and show no tendency to plug, the total vacum for the whole system registered at the exhauster end should be about 8 to 12 inches of Hg.

When the brine has been pretreated, operation in the distiller and vat house becomes very simple. The plugging of the apparatus and piping by mud will have completely disappeared and there is very little need for changing over to the standby unit for cleaning. Operation is less likely to be interrupted, and the capacity of the system in terms of soda ash output can be greatly increased.

Tower house. The main units in the tower house are the carbonating columns and the filters, and the control tests as made in the field are out-

lined below. In the green liquor line to the columns, a thermometer pocket should be provided to receive a thermometer for measuring the temperature of the green liquor to the towers. This temperature should be not more than 30° C., a higher temperature causing excessive volatilization of ammonia from the top of the towers and putting heavier duty on the tower washers. The green liquor is tested for NH_3 and Cl^- titers. Their respective concentrations and relative titers should have the values given in Chapter VII, *i.e.*, 98 to 99 titers for NH_3 and 89 to 90 titers for Cl^-. These titers should not differ by more than 1 or 2 units from day to day, as with a large capacity in the vats there should not be any difficulty in maintaining a constant strength of the ammoniated brine. The percentage of carbon dioxide in the mixed gases to the towers should be analyzed with an Orsat. According to the efficiency of the plant, this carbon dioxide percentage in the mixed gases will vary from 53 to 60 per cent. Similarly the waste gases· from the top of the towers should be tested with an Orsat. For the making towers, the percentage of carbon dioxide should be from 3 to 5 per cent by volume, while for a cleaning tower it should be about 1 per cent. It is evident that the lower the percentage of carbon dioxide in the waste gases, the better the tower absorption efficiency for carbon dioxide, and the smaller the loss of carbon dioxide. For a cleaning tower the outlet liquor is tested for carbon dioxide content by means of a simple evolution method (Fig. 124, Chapter XXVIII). There should be 61 to 66 cc. per 2 cc. of the liquor corresponding to 60 to 65 grams of carbon dioxide per liter.

Temperature regulation in the columns is vital to their successful operation. The point about two-thirds of the height of the tower should be provided with a thermometer pocket to ascertain the reaction temperature in the towers. This reaction point happens to be near the tower-working (or draw) floor or one floor above so that the reading can be readily taken there. It is above the cooling section of the tower and should have a temperature of 55° to 60° C. But unless there is full decomposition reaction in the towers, such a temperature cannot be developed. And unless the temperature is high here, good crystals of bicarbonate cannot be obtained at the bottom. Consequently. while it is necessary to get full cooling effect at the bottom of the tower, a part of the cooling water must be "bled out" from the middle of the cooling sections to permit the top portion of the cooling sections of the column to remain at a comparatively high temperature. A continuous temperature gradient in the towers is thus maintained, whereupon the bicarbonate crystals may build up as the liquor is cooled. In a column having an ample cooling surface and a long path of travel for the cooling water, the top cooling water outlet temperature should be around 45° C. Consequently, the cooling water outlet temperatures as well as the temperatures at the two-thirds point of the tower and at the draw must be closely observed. One thermometer each is provided in the top and in the middle (bleeding) cooling water outlet points to observe the temperature of the cooling water and adjust the amount of bleeding.

The tower draw temperature should be frequently tested at the draw funnel (every 5 to 10 minutes) and a portion is taken in a 100 cc. measuring cylinder to ascertain the quantity (percentage by volume) of the bicarbonate in the draw liquor and to observe the number of minutes the bicarbonate takes to settle out with a sharp boundary between the crystals and the supernatant liquor. With good crystals it should not take more than 3 minutes to settle. Poor bicarbonate crystals may take considerably longer time and give a milky precipitate with an ill-defined and mobile boundary between the precipitate and the clear liquor. A 5-cc. portion of this clear liquor is pipetted off and titrated for "free ammonia" with N H_2SO_4, using methyl orange as the indicator. The same portion after "free ammonia" determination can be titrated for Cl^- by Mohr's method with the addition of a small amount of calcium carbonate powder to neutralize the acidity. It should be noted that the "free ammonia" determination is in reality a total alkali titration and the result, strictly speaking, does not represent free ammonia alone, but the error is on the safe side. With the ammonia and chlorine titers known in the green liquor and with the "free ammonia" determined in the draw liquor, the tower decomposition, *i.e.*, per cent conversion, can be roughly estimated as follows:

$$\% \text{ Decomposition} = \frac{\text{NH}_3 \text{ titer in green liquor} - \text{free NH}_3 \text{ titer in draw liquor}}{\text{Cl}^- \text{ titer in green liquor}} \times 100$$

This is only a rough indication of more or less relative value to the operators for the reasons mentioned and also because it does not take into account the change in volume between the green liquor and the draw liquor and the loss of ammonia from the towers to the tower washers.

At the filters the head of wash water above the orifice should be regulated. No attempt is made to make any chemical determination on the bicarbonate in the field. The filter liquor in the filter liquor drop leg from the filter separator to the main is sampled for a Cl^- determination. From the Cl^- titer in the draw liquor and that in the filter liquor, the amount of dilution by wash water on each filter can be readily ascertained. At other points in the filter liquor main where other solutions are introduced similar Cl^- determinations are made to determine the amount of dilution in the filter liquor at these respective points. The furnace gas, after passing through the condensers on its way to the compressors, is scrubbed and cooled by soft water in a scrubbing tower and the wash water is circulated in this scrubber by a centrifugal pump, until a titer of 8 to 10 is reached or until the water gets too warm. This wash water carrying ammonia may be used for filter wash. The wash water in the scrubbing tower is titrated for ammonia content in order that neither too much fresh water may be added nor too high an ammonia concentration in the wash water may be reached. The amount of cooling water through the furnace condenser is adjusted, so that ammonium carbonate crystals may not be formed as the result of the temperature in the condenser getting too low.

With the insertion of a furnace gas scrubber before the condenser, however, there is little occasion for trouble arising from this source.

Distiller house. The milk of lime for the distiller should be titrated for total lime. It is important to make as concentrated a milk of lime as can be handled in the piping system. Too weak a milk of lime will cause unnecessary dilution of the liquor to be distilled, resulting in the waste of steam, loss of ammonia and loss of lime as excess lime in the large volume of distiller waste produced.

For the same reason, it is even more important to keep the filter liquor as concentrated as possible. Waste liquor should be kept small in volume and floor wash water should not find access to the filter liquor system. A dilute feed liquor puts a very heavy load on the distiller, making it very difficult to make the required quantity of ammoniated brine in the absorber. This is a serious matter, because so large a volume of dilute feed liquor would have to be put through the distiller that the several compartments at the bottom of the distiller would tend to be filled up, making the steam pressure at the bottom compartment excessive and the top temperature of the distiller fall off. This always results in heavy loss of ammonia in the distiller waste or run-off liquor. Consequently in a large alkali works a special weak ammonia distiller is provided for distilling off the various weak ammonia-bearing liquors.

On the top of the distiller, there should be a recording thermometer to register the temperature of the exit ammonia gas. There a manometer should also be provided to adjust the pressure condition (vacuum) in the distiller. The distiller top should have a vacuum of about $\frac{1}{4}$ cm. Hg, both to prevent any possible leakage of ammonia to the room and to aid the distillation of ammonia gas from the distiller. The temperature should be about 82° to 86° C., but this temperature is dependent upon the individual construction of the distiller and the location of the distiller condenser in the system. Similarly the distiller condenser outlet should be provided with a thermometer and a mercury manometer. The temperature of the ammonia gas at the outlet of the condenser to the absorber should be above 55° C. and the vacuum about 1.5 cm. Hg. If the temperature of the outlet gas from the distiller condenser is much above 55° C., excessive steam would pass on to the absorber, causing dilution of the ammoniated brine (low Cl⁻ titer), and also poor ammonia absorption in the absorber (high temperature in absorber). This frequently leads to the "hot top" phenomenon in the absorber and is detrimental to the absorber operation. On the other hand, if the distiller condenser outlet gas temperature is below 55° C., ammonium carbonate and ammonium carbamate crystals tend to form in the gas passage, clogging the condensers. The heater liquor, *i.e.*, liquor from the bottom of the heater before entering the pre-limer or lime still, should be tested for free ammonia and carbon dioxide. The carbon dioxide, as in the cleaning tower liquor, is determined by the simple evolution method, and the volume similarly recorded. There should be little or no carbon dioxide, but there will be some free ammonia in the heater liquor in the type of arrangement in which the heater is

placed directly over the lime still with strong ammonia gases from the lime still below passing in contact with the liquor from the heater. The heater temperature should be closely observed. Too low a temperature will cause incomplete removal of carbon dioxide gas from the heater, and too high a temperature will add an unnecessary burden to the condensers above. The distiller waste should be tested for the presence of excess lime by titrating with hydrochloric acid. The complete removal of ammonia from the distiller waste can be ascertained by the sense of smell, which is delicate enough to guide the operation provided a sufficient excess of lime has been maintained. A Nessler reagent is kept at hand to test ammonia whenever desired. The milk of lime and filter liquor are both fed to the distiller through orifices whose diameters and liquor heads above the respective orifice plates should be recorded. The amount of milk of lime used should be in proportion to the quantity and the fixed NH_3 titer in the filter liquor feed. With the strength of the milk of lime and the composition of the filter liquor to the distiller running uniform day and night, this relation will soon be established. In normal operation, there is to be added a volume of milk of lime equal to about a third of the volume of filter liquor fed. The prelimer liquor should be tested for free ammonia and excess lime. To study the dilution of mother liquor by wash water, furnace condensate, etc., samples of filter liquor are taken at different points and the Cl⁻ titers determined. The volume is inversely proportional to the concentration or titer of chlorine. The exhaust steam main to the distiller should be provided with a recording pressure gauge and the distiller bottom compartment with an ammonia-proof pressure gauge. The pressure at the bottom compartment of the distiller varies from 8 to 10 pounds, depending upon the individual construction of the lime still and the heater, and the rate of operation. When the distiller shows plugging or when the volume of the liquor in the distiller for some reasons is excessive, the pressure may rise to even 12 to 15 pounds. The distiller bottom compartment should be provided with an ammonia meter (such as an Esterline-Angus recorder) to indicate the presence of ammonia in the distiller waste, by means of conductivity measurement, using a recording ohm-meter. The meter may be calibrated in dollars of ammonia loss per ton of soda ash to impress the distiller men.

Furnace room. The furnace gas up-take should be provided with a water manometer to indicate the pressure (vacuum) condition inside the furnace. The nearer the furnace approaches the neutral condition, the better it is for the furnace operation and furnace gas obtained. Too high a vacuum causes much leakage of air inward and consequently a weak returned gas. Too high a positive pressure would cause steam to condense in the returned ash chute and in the extract barrel, clogging these passages. It may even cause blowing through the extract barrel. The flue gas up-take or down-take, as the case may be, at the extract end of the furnace should be provided with a base-metal thermocouple with a recording meter to show the temperature of the flue gases. This flue gas temperature

may be from 350° to 450° C. The extract ash is tested for temperature every few minutes. The temperature should be between 175° to 190° C.

These extract and flue gas temperatures, especially the former, give indications whether the bicarbonate in the ash is all out. These are not always absolutely reliable. They are reliable when the furnace is operating uniformly, *i.e.*, when it is charged and discharged regularly and continuously. When, however, the discharge is interrupted for some reason, the ash that first comes out may be completely free from bicarbonate, and yet has a lower temperature than it should; on the other hand, when the furnace is pushed too hard, the fire being pulled forward toward the extract end by the stronger draft employed, with the ash pouring out through the extract, not all the bicarbonate will have been decomposed in the extract, though the extract temperature does not appear particularly low. With some experience, the operator can judge unmistakably whether the ash is free from bicarbonate. The ash that has been completely calcined looks powdery and "dead." The ash that contains undecomposed bicarbonate looks mobile and flows like a fluid. The furnace condenser gas outlet should be provided with a thermometer and the cooling water regulated according to this outlet temperature. The temperature of the gas here should not be below 30° C. and the use of a furnace gas scrubber greatly lessens the duty of the furnace gas condenser, and consequently the amount of cooling water required for this condenser would not be large. In the furnace gas system, as in the lime kiln gas system or in the absorber vacuum system, manometers are provided at various points to follow the vacuum conditions and to observe any plugging tendency caused by soda dust at any point in the system. This trouble is very likely to occur in the gas up-take main between the furnace gas outlet and the furnace gas scrubber, because of soda dust deposition carried over in the furnace gas. Butterfly valves are provided to control the vacuum conditions in the furnaces. In the main, beyond the gas scrubber an automatic vacuum regulator should be provided operating on the gasometer principle for maintaining a constant pressure in the dryer. Chemical examinations, either on the bicarbonate fed to the furnace or on the extract ash from the furnace, are not attempted by the operators in the field, but the temperature of the extract is closely observed to insure a completely calcined ash.

The amount of returned ash is judged by the wetness of the bicarbonate and by the behavior of the furnace, *i.e.*, scaling in the furnace. The bicarbonate from the filter should not ooze out moisture on continued kneading in the hand. The returned gas should be analyzed for the percentage of carbon dioxide with an Orsat. The ability to get a large output from the towers, other conditions being equal, will depend upon the richness of the gas returned from the furnaces. Not only the capacity of the columns but also the crystalline character of the bicarbonate obtained—in fact the whole successful operation of the towers—will be largely contingent upon the richness of the gas from the furnaces. The ash coming from the furnace is cooled in an ash cooler to 80 or 70° C. and should be

packed hot so that the ash may not absorb excessive moisture from the air. The ash as packed is sorted according to the color and grade, and classified into a number of grades in accordance with market conditions. Normally there is only one grade, however.

Power plant. In the boiler room, the coal burned in the furnace should be weighed and also the ash coming from the furnace. The pressure of the steam in the boilers should be recorded. It is desirable to have a meter inserted in the feed line to measure the water fed to the boilers. The temperatures of the feed water entering and leaving the feed water heater should be recorded to determine what the heater is doing. Tests for oxygen content in the feed water from the deaerating heater to the boilers should be regularly made and recorded. A draft gauge should be installed at each furnace to regulate the draft to be carried by the boiler. A carbon dioxide recorder will pay for its own installation. On the steam main taking steam from a battery of several boilers there should be a steam flow meter to measure the quantity of steam generated per hour, and a recording pressure gauge to register the average pressure of steam during the 24 hours. In the engine room, there should be a complete record of the voltage, current, kilowatt hours, etc. of the generators, and the current in each feeder supplying power to each house in the plant. A complete set of control instruments, such as frequency meter, power factor meter, voltage regulator, synchroscope, and standard power plant accessories, should also be provided. On the carbon dioxide compressors, the vacuum exhausters, the air compressors, and the main cooling water pumps (all these large units being steam driven to get the exhaust steam required) the r.p.m.'s, the pressures (or vacua), and the temperatures at each gas inlet and outlet should be observed and recorded. The fewer the number of r.p.m.'s in the carbon dioxide compressors for a given plant output, the better will be the power economy, as this means smaller consumption in coal. The titer of soda water for lubricating CO_2 gas valves and cylinders should be determined at least twice a week. The sodium carbonate content in the soda water used should have about 10-12 titer.

All samples which the operatives cannot test in the field are taken care of by the chemical laboratory. Samples of the liquors or solid products (as the case may be) must be taken at regular intervals as directed by the chief chemist and a composite for each during the shift sent to the laboratory daily for analysis. This applies to all samples whether the operatives are required to test in the field or not.

The smoothness of operation depends upon delicate control and absolute regularity of operation. The process permits of no interruption in any part of the process for 24 hours a day and 365 days a year. If, in a certain apparatus, *e.g.*, the towers, the operation of the carbon dioxide compressors is suddenly interrupted for some reason, it means that the columns will be plugged solid, which may put them out of commission for days. Another requirement is that the operation in all divisions be balanced, as the process depends upon the interworking of the several

divisions. Trouble in any one division will soon be reflected in the others and the whole plant may be thereby crippled.

Table 147 gives an estimate of the cooling surface necessary in each apparatus per ton of soda ash expected from the said apparatus. No hard and fast rule, however, can be laid down.

TABLE 147. Cooling Surface Required.
(For average conditions.)

Apparatus	Cooling Surface Required per Ton of Soda Ash Made
Vat coolers	80-120 sq. ft.
Carbonating towers	75-90 sq. ft. in each tower
Distillers	
Coolers on top of the distiller with filter liquor	40 ⎰Total
Condensers for NH$_3$ gases with water	30 ⎱70 sq. ft.
Absorber coolers	⎰25 sq. ft. for liquor ⎱ Total ⎱15 sq. ft. for gases ⎰ 40 sq. ft.
Furnace condensers	30 sq. ft.

With good cooling water, the amount of cooling surface provided for each unit is ample. Nevertheless, specific conditions in each individual plant may vary so that considerable departure from the cooling surface given is possible.

Chapter XXVI

Losses and Consumption of Raw Materials in Ammonia Soda Process

While the ammonia soda process is capable of the highest scientific control and is being conducted exceedingly well, the efficiency of the main operation, the conversion of sodium chloride into sodium bicarbonate, by the nature of the reaction, is unfortunately comparatively low. The average figure for the decomposition of sodium chloride to sodium bicarbonate is below 75 per cent. Under the best conditions even for a short time, the percentage of conversion of sodium chloride falls short of 80 per cent. This is quite different from the usual efficiency of 95 or even 98 per cent in most of the other chemical industries. This low efficiency has been so far tolerated because salt is cheap and is a small item in the cost of soda manufacture. In certain plants salt is recovered from the distiller waste as refined salt. Operators in the plant are too accustomed to look upon the losses of salt with little concern, although their vigilance in safeguarding the process from loss of ammonia has been most particular. As a general rule in the plant, an effort is made only to recover ammonia, other constituents, such as salt, etc., being discarded as distiller waste.

In the manufacture of ammonia soda, the direct raw materials are salt and limestone. Ammonia may be compared to a catalyst, but its loss in the cycle of operation is virtually chargeable to its consumption by the process. Coal and coke may be regarded as indirect raw materials. We shall now enumerate the sources of losses of different raw materials in the process and give normal figures, wherever possible, for the rate of consumption of each according to the best modern practice.

Carbon dioxide.

All carbon dioxide that goes to make soda ash is derived from limestone. Lime, the joint product from the burning of limestone, is used in the recovery of ammonia. The rate of limestone consumption is governed by the rate of consumption of lime and carbon dioxide gas. Generally, however, it is the lime, rather than the carbon dioxide gas, that determines the consumption of limestone in the plant. But the loss of carbon dioxide, especially the richer carbon dioxide gases (either from the wastage of the rich gas or from the dilution of the gas by air, thereby rendering the carbon dioxide less available) has an important bearing on column operation and consequently causes a higher rate of consumption of all materials—salt, ammonia, coal, limestone and coke. The sources of loss of carbon dioxide are as follows:

(a) **Leakage on the top of the lime kiln.** The top of the lime kiln is usually not gas-tight, and any attempt to run the kiln under vacuum to aid the decomposition of limestone generally results in a low test gas caused by air leakage from without. Consequently, we are compelled to run the kiln with a slight positive pressure at the top. Hence there is a considerable loss of carbon dioxide from the kiln to the atmosphere. Fortunately this is a "lean" gas and its loss is not seriously felt. Generally there is an excess of this "lean" gas which is allowed to escape to the atmosphere through the vent pipe provided on top of the kiln.

(b) **Formation of calcium carbonate with milk of lime in the distiller.** If the heater is not working efficiently, not all the carbon dioxide in the liquor will be driven out. Even in a distiller of good design, considerable carbon dioxide at times may be found in the liquor at the bottom of the heater. The loss, however, should be very small and should not be tolerated when found in considerable quantities, as it means a corresponding loss in available lime.

(c) **Formation of calcium carbonate and magnesium carbonate in the absorber and vats.** Carbon dioxide gas coming over with ammonia from the distiller is dissolved by brine in the absorber, forming ammonium carbonate, etc. If the brine contains impurities such as calcium sulfate, as in rock salt brine, or calcium and magnesium sulfates and chlorides, as in sea brine, corresponding calcium and magnesium carbonates are formed, constituting a large part of the "mud" in the vats. This gives rise to the presence of fixed ammonia in the ammoniated brine. The extent to which fixed ammonia occurs depends upon the amount of these impurities in the brine used. Generally, it would be about 3 to 5 titer and may be as high as 8 titer for sea brine. This generally amounts to 2 to 3 per cent for the loss of carbon dioxide on the weight of carbon dioxide handled. (See Chapter V, "Purification of Brine.").

(d) **Exhaust from absorber vacuum pump.** Just as ammonia is recovered from the mother liquor from the columns by distillation, so also the carbon dioxide dissolved in the mother liquor is recovered in the distiller. Normally with strong ammonia gas, carbon dioxide ought to be absorbed by the resulting ammoniated brine. But as the temperature in the absorber bottom and in vats is about 65° C. the partial pressure of carbon dioxide in the hot ammoniated brine is considerable. Considerable carbon dioxide will escape from the ammoniated brine. In the absorber washer and weak washer, the outlet gas from the absorber and from the vat vent lines containing ammonia and carbon dioxide is deprived of all its ammonia content, leaving most of the carbon dioxide as spent gas to be drawn through to the vacuum pump or exhauster. Except for the small quantity of air leaking into the system, this exhaust gas should be essentially carbon dioxide. If the absorber system is air-tight, the percentage of carbon dioxide in the exhaust gas should be considerably higher than that of the kiln gas. It may test around 70 per cent carbon dioxide. The gas should be sent back to the tower gas main and made available for tower operation. If the absorber system permits leakage of air

through the pipe joints, manometer connections, valve packings, cover flanges, etc., the exhaust gas may contain less than 20 per cent carbon dioxide, and the gas is thus absolutely worthless and has to be discharged to the air. The loss here is 10 to 15 per cent of the rich gas available. Such a loss cannot be tolerated if the soda plant is to be run efficiently. Some sulfide is also recovered along with this absorber gas.

(e) **Exhaust from the filter vacuum pump.** Because of the high vacuum employed there is a tendency to suck out carbon dioxide and ammonia from the mother liquor in the filters. As a large quantity of air is sucked in through the pores in the filtering medium, carbon dioxide in the exhaust of the filter exhauster is very weak, and has to be discharged to the air. Fortunately, because of the lower temperature of the draw liquor, the loss of carbon dioxide is not serious and should be very small.

(f) **Exit gases through the column washers.** The column washer is designed to scrub ammonia from the spent gas from the carbonating columns. All the carbon dioxide is lost. The amount of loss is determined by the efficiency of the carbon dioxide absorption in column operation. Normally it should be less than 5 per cent of the total gas pumped to the columns. A general mathematical formula in terms of the percentage of carbon dioxide in the mixed gases into the columns and the percentage of carbon dioxide in the column exit is given below:

$$\text{Let } P_m = \% \; CO_2 \text{ by vol. in the mixed gases to the columns}$$
$$P_e = \% \; CO_2 \text{ by vol. in the column exit gas}$$
$$L = \% \text{ loss of } CO_2$$

$$\text{Then } L = \frac{\dfrac{P_e}{100 - P_e}}{\dfrac{P_m}{100 - P_m}} \times 100 = \frac{P_e \, (100 - P_m)}{P_m \, (100 - P_e)} \times 100 \tag{1}$$

If the mixed gases in the columns are approximately 50 per cent, $100 - P_m$ is nearly equal to P_m. As P_e is small, generally less than 5 per cent, $100 - P_e$ can be cancelled by 100. In such cases P_e can be taken roughly equal to L, the percentage loss of carbon dioxide from the total carbon dioxide admitted to the columns. Good Solvay columns should have a carbon dioxide absorption efficiency of more than 95 per cent.

(g) **Carbon dioxide blown from soda furnaces.** Normally the calcining furnace is run under a very small vacuum or, better still, under exactly neutral conditions of pressure. There should not be much loss of carbon dioxide gas. But due to pressure fluctuations in the furnace and the unavoidable opening of the barring hole for chiselling the scale, etc., sometimes the furnace gases are blown or puffed out. When the furnace is not running smoothly because of scale formation, poor bicarbonate crystals, or excessive moisture content in the bicarbonate, there is sometimes a momentary pressure inside the furnace causing a loss of the seal in the barrel extract or feed passages, and the gases containing ammonia, carbon dioxide and soda dust may be blown out through these openings.

In normal running, however, such cases seldom occur and the loss of carbon dioxide should not be large.

Any loss in carbon dioxide will have to be made up by increasing the rate of burning of the limestone in the lime kiln. As the carbon dioxide obtained in this way is in a comparatively dilute form, the increase in the volume of the kiln gas relative to the volume of the rich gas from the dryers and from the absorber system reduces the average percentage of carbon dioxide in the mixed gases. This, as has been shown in Chapter VIII, is a very serious drawback in column operation. Let us examine this point further. Let

V_k = Vol. of kiln gas and P_k its CO_2 concentration expressed as a fraction by vol.
V_f = Vol. of furnace gas and P_f its CO_2 concentration expressed as a fraction by vol.
P_m = CO_2 concentration in the mixed gases expressed as a fraction by vol.

Then

$$P_m = \frac{V_k P_k + V_f P_f}{V_k + V_f}$$

$$P_m V_k + P_m V_f = V_k P_k + V_f P_f$$

or

$$(P_m - P_k) V_k = V_f (P_f - P_m)$$

or

$$\frac{V_k}{V_f} = \frac{P_f - P_m}{P_m - P_k} \tag{2}$$

That is, the ratio of the volume of the kiln gas to the volume of the furnace gas is as the difference in carbon dioxide concentrations between the furnace gas and the mixed gases is to the difference in carbon dioxide concentrations between the mixed gases and the kiln gas. Again from (2)

$$\frac{P_k V_k}{P_f V_f} = \frac{P_k (P_f - P_m)}{P_f (P_m - P_k)}$$

Adding the numerator to the denominator on each side,

$$\frac{P_k V_k}{P_f V_f + P_k V_k} = \frac{P_k (P_f - P_m)}{P_m (P_f - P_k)} = \frac{\dfrac{P_f - P_m}{P_m}}{\dfrac{P_f - P_k}{P_k}} = \frac{\dfrac{P_f}{P_m} - 1}{\dfrac{P_f}{P_k} - 1}$$

$\therefore$ Given P_k, P_m, P_f, let x = the fraction of CO_2 (by weight) contributed by the lime kilns in the mixed gas to the columns

$$x = \frac{\dfrac{P_f}{P_m} - 1}{\dfrac{P_f}{P_k} - 1} \tag{3}$$

Therefore if we know the concentrations P_k, P_m, P_f, we can readily find out the amount of CO_2 (by weight) furnished by the lime kilns or by the dryers.

An interesting case presents itself when the kilns and the furnaces furnish equal amounts (weights) of CO_2 for the tower operation, in which case

$$P_f V_f = P_k V_k$$

$$\therefore \frac{P_k}{P_f}\left(\frac{V_k}{V_f}\right) = 1 = \frac{P_k}{P_f}\left(\frac{P_f - P_m}{P_m - P_k}\right) \text{ from (2)}$$

$$\therefore P_k P_f - P_k P_m = P_f P_m - P_f P_k$$

$$\therefore P_m = \frac{2 P_k P_f}{P_k + P_f} \tag{4}$$

This relation can also be obtained by putting $x = \frac{1}{2}$ in (3) above. That is, in the ideal case where there is no loss of carbon dioxide gas and when the furnace operation is in step with the column operation, so that the lime kilns and the furnaces furnish equal amounts of carbon dioxide to the columns, the percentage of carbon dioxide in the mixed gases forms a *harmonic mean* between the percentage of carbon dioxide in the dryer gas and the percentage of carbon dioxide in the kiln gas. This relation affords a good guide in operation. When the furnace gas contains 90 per cent carbon dioxide by volume and the kiln gas 41 per cent, and when both contribute equal amounts of carbon dioxide to the column operation, then

$$P_m = \frac{2 \times 0.41 \times 0.90}{0.41 + 0.90} = 0.563 \text{ or } 56.3\% \text{ from (4)}$$

But as is often the case, the furnaces contribute only 45 per cent of the total carbon dioxide required for the column operation and the lime kilns 55 per cent, then from (3)

$$0.55 = \frac{\dfrac{0.90}{P_m} - 1}{\dfrac{0.90}{0.41} - 1} \quad \therefore P_m = 0.542 \text{ or } 54.2\%$$

This gives normal figures for the column mixed gases. But when the furnaces are furnishing 55 per cent and the lime kilns 45 per cent, the mixed gases will test higher and their value then becomes 58.5 per cent.

If, under close control, the furnace gas tests 95 per cent CO_2 by volume and the kiln gas 42 per cent CO_2, if the two sources contribute equal amounts of carbon dioxide for column operation, then the percentage of CO_2 in the mixed gases will be

$$P_m = \frac{2 \times 0.42 \times 0.95}{0.42 + 0.95} = 58.2\%$$

If, as may happen, the furnaces contribute 60 per cent of the total CO_2 to the columns, then

$$.40 = \frac{\dfrac{.95}{P_m} - 1}{\dfrac{95}{42} - 1} \quad \therefore P_m = 63.1\%$$

In practice, because of other minor sources of comparatively rich CO_2 gas, such as the absorber exhauster discharge, etc., the mixed gases to the columns may frequently average more than 60 per cent CO_2. Momentary readings may go as high as 67 per cent, but they are not the average. On the whole, per cent CO_2 by volume in the mixed gases to the columns cannot exceed 60 per cent by volume under normal working conditions. This is the argument in favor of the "double entry" arrangement, whereby the original 90-95 per cent richness in the furnace gas can be utilized.

In the final analysis, all losses of CO_2 must be made up from the burning of limestone in the kiln.

It will be seen from the foregoing discussion that the loss of carbon dioxide (if the absorber exhauster gas is returned to the columns), should be from 15 to 20 per cent of the total carbon dioxide handled. Theoretically, to make enough sodium bicarbonate for 1 metric ton of ash, there is required a volume of 422 cubic meters of pure carbon dioxide under standard conditions. Assuming a total loss of 17 per cent, the volume of carbon dioxide under standard conditions would be 509 cubic meters per ton of ash. At an average of 57.5 per cent carbon dioxide in the mixed gases in the columns, at a temperature of 30° C. and at a vacuum of 2 inches H_2O, assuming a volumetric efficiency of 80 per cent in the carbon dioxide compressor cylinders, there will be required 1230 cubic meters of piston displacement in the gas cylinders per ton of ash.

Ammonia.

One of the greatest achievements made in the ammonia soda industry today is the high efficiency of the ammonia cycle. In contrast to a loss of ammonia of 50 to 80 kg. of ammonium sulfate per 1000 kg. of soda in 1880, today's figure of 3 to 4 kg. of ammonium sulfate per 1000 kg. of soda ash for small plants and still less for large plants marks a good step of advancement. Of course, the modern soda plants have an advantage in that they work on a very much larger scale and the loss of ammonia per unit of production is necessarily smaller. Following are possible sources of loss of ammonia:

(a) **Ammonia stills.** Considerable effort is now directed to keeping the volumes of the filter liquor and milk of lime for the distiller at a minimum. There are various reasons why the volume of the liquors fed to the distiller should be kept as small as possible. One reason is to reduce the loss of ammonia through the distiller. In the distiller waste there is always a small amount of ammonia that has not been completely distilled out. The removal of the last portion of ammonia remaining in solution requires a long time. Generally, not less than 0.005 gram of ammonia per liter is present in the distiller waste. At the rate of 10 cubic meters of distiller waste per ton of ash, there is a loss of ammonia of at least 0.2 kg. ammonium sulfate per ton of ash. This does not include losses caused by an accidental "sour bottom," or by a momentary deficiency in lime causing fixed ammonia in the distiller waste, or by

other accidents. Under the best conditions, the distillers are one of the largest sources of loss of ammonia in the whole soda ash plant.

(b) **Dryers.** Considerable ammonia may also be lost in the form of gases leaking from the soda dryers. The dryers are never gas-tight at rotating joints, etc., and frequently there is need to open a hole for rodding or chiselling the scale. The loss is considerable when an attempt is made to run the furnace under a slight pressure to maintain a good gas test. Hence a very slight vacuum is desirable, consistent with a good gas test.

(c) **Tower washers.** The function of the tower washer is to scrub ammonia from the tower exit gases with saturated brine which is to be later sent to the absorber for ammonia absorption. Under normal running conditions with an ammonia titer not over 12 in the bottom compartment of the tower washer, using cold, saturated brine, the loss of ammonia through the tower washer is small. When the mixed gases to the columns are low in carbon dioxide, when the carbon dioxide absorption in the carbonating columns is poor, when the column decomposition is low, when the green liquor fed to the top of the carbonating column is at an excessive temperature, and when the saturated brine used for scrubbing cannot be kept cold, as is the case during the hottest summer days, then the volume of brine is not sufficient to scrub the ammonia in the column exit gases and the loss of ammonia may be considerable. The body of the column washer will then be hot and ammonia cannot be readily kept in solution. As the quantity of the saturated brine that can be put through the column washers is limited by the rate of production, *i.e.*, by the rate of ammonia distillation, it would not be feasible to let down a larger stream of brine to the top of the column washer than can be used in the system. Losses under these conditions cannot be ascertained except by observing the total losses over a period of time by means of a gas meter measuring a small stream of the column washer exit gas and determining the quantity of ammonia by an absorption bottle.

(d) **Absorber and filter exhausters.** The duty of the filter washer is generally light. Unless the design of the washer is faulty, or the brine used for scrubbing is at an undesirably high temperature, there is little loss of ammonia in the filter exhaust. In the absorber exhauster, however, there is danger of losing ammonia during the "hot top" time. When, however, the exhaust gas is sent back to the columns, as should be the case, such a danger does not exist. This is one of the reasons why the exhaust gas from the absorber system should not be discharged to the atmosphere and every effort should be made to stop air leakages in the absorber vacuum system to enable the gas to be returned to the column gas main.

(e) **Draw funnel and bicarbonate filters and exposed bicarbonate on the feed floor in the furnace room.** It has not been found successful to have the ammonia liquors going through the process in a closed system throughout, *i.e.*, without exposing any portion of the liquor at any stage to the open air. Under the present method of working the slerry, the

magma is drawn from the carbonating columns and exposed to the air at the receiving funnel and at the filters. At a low draw temperature and with good decomposition, little odor of ammonia is noticed in the room and the loss of ammonia is negligible. When, however, the decomposition of the sodium chloride in the columns is low, when the free ammonia titer is high, and when there is not enough cooling in the columns to operate them at a low draw temperature, considerable ammonia is lost to the air from the warm liquor, when the liquor is drawn out to the draw funnel and exposed at the filters. Not only does this mean a loss of ammonia but it also causes inconvenience to the workmen in the room, a condition that spells failure for the plant.

(f) **Piping connections, gasket flanges, pump packing glands, valve and cock packings, manometer connections, sampling pipe nozzles, etc.** The minor losses of ammonia liquors caused by leaks in the centrifugal and plunger pump packing glands, leaky valves and cocks, manometer connections, sampling lines, etc., though much to be regretted, are to a certain extent unavoidable, as the corrosion and wear on the materials by ammoniated brine liquors at an elevated temperature create a problem which still confronts ammonia soda manufacturers. In a poorly managed plant, the loss of ammonia from leaks everywhere and from let-outs may far exceed the normal loss in the distillers. The total loss may be so great that it is hardly possible to account for the depletion of ammonia in the system. A search for the sources of loss must be made and the conditions immediately remedied. On the floors of each of the rooms where such pumps are located or where such liquors are likely to be spilled, there should be provided a sump to collect these ammonia-bearing waste liquors which are to be immediately returned to the weak liquor distiller for distillation. In plants where the volume of the liquor handled is large, these minor losses are insignificant. In a small plant having a small output such losses may amount to quite an item.

Theoretically, according to the reaction

$$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$$
$$\downarrow$$
$$\frac{1}{2}(Na_2CO_3 + H_2O + CO_2)$$
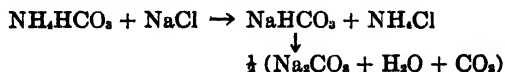
to make 1 ton of ash there would be required 0.32 ton of ammonia to be distilled. In practice, however, owing to the presence of considerable free ammonia in the draw, at least 0.45 ton of ammonia must be circulated, *i.e.*, the ammonia efficiency in the towers is below 75 per cent on the average. Every handling of ammonia is accompanied by some loss: therefore, for a given output in soda ash, the higher the ammonia efficiency in the columns, the smaller the quantity of ammonia circulated, the less is the ammonia loss, other conditions being equal.

(g) **Tube leaks.** Cooling-tube leaks at the tube sheets in the strong liquor coolers or gas condensers are likely to occur even if cast-iron cooling tubes are used. Cast-iron tubes in the distiller condensers are known to have been eaten through by hot ammonia gases after five years in

service. To check these leaks, the exit cooling water is occasionally tested for ammonia. To follow any loss, sewer samples taken around the plant are frequently tested for ammonia.

In order to maintain the absolute regularity of operation which is required in the working of the ammonia soda process, the rate of operation in the various divisions must be held constant. Since the settling and storing capacity in the vats and storage tanks is practically constant, the soda ash output of the plant depends upon how fast the ammoniated brine can be circulated, i.e., from the absorber, through the towers, through the distillers, and back to the absorber. This, in turn, depends upon how many hours the ammoniated brine takes for complete settling in the vats. For the speed with which the ammoniated brine can be sent through the system is mainly governed by how fast it can be put through the settling vats to get a complete settling. The settling capacity of the vats and the storage capacity of strong liquor storage tanks have an important bearing on the ultimate rate of production. Generally, with a high quality brine containing small amounts of impurities, there should be capacity enough in the settling vats and in the storage tanks to hold the volume of ammoniated brine in the form of stock and working liquors of normal strength equivalent to at least as many tons of ammonia (calculated as $(NH_4)_2SO_4$), as the daily tonnage output of soda ash in the plant. This figure varies greatly according to the purity of the brine available. With the present day brine pretreatment, the ammoniated brine settling and storage capacity can be greatly reduced.

Lime.

Limestone is one of the important raw materials in the ammonia soda industry, as it furnishes all the carbon dioxide required for soda ash manufacture and all the lime for the recovery of the comparatively expensive material, ammonia, and also lime for causticization. Theoretically, one molecular weight of limestone is required for every molecular weight of soda ash viewed from the standpoint either of the calcium oxide or of the carbon dioxide entering into the reaction. But because of various losses, some of which are unavoidable in practical operation, the consumption of lime and consequently of limestone is greater.

The sources of loss of lime or limestone are as follows.

(a) **Waste in breaking.** In breaking and crushing the limestone to the required size of 5 to 6 inches, there are always some fine pieces smaller than 2 inches. These have to be screened out and discarded, although the fines may be valuable for concrete construction work, road pavement, etc., and high silica stone may be useful in the cement manufacture.

(b) **Underburned or unburned limestone.** In order to get a high test gas, no more coke than necessary is charged with the stone in the kiln. Sometimes, intentionally, slightly less coke is used than is necessary to burn the stone completely, and there will be some underburned core in the lime drawn. The amount of unburned stone in the lime is 5 to 10 per cent. Although unburned stones of the sizes above 2 inches are returnable to

the kiln as returned stone, the smaller sizes of unburned stone are rejected as "sand" and the fines which are suspended in the milk of lime simply pass through the distiller and out in the distiller waste. The total loss is estimated to be about 2 to 3 per cent. It is apparent that the unburned stone generally comes from that portion of the stone that is of the poorer grade, which is less readily decomposed, unless the fuel and air distributions in the lime kiln are faulty.

(c) **Overburned or dead-burned lime.** There is frequently a small amount of overburned lime in the draw, even when the fuel ratio is not excessive. This overburned or dead-burned lime takes a long time, sometimes days, to become hydrated or slaked. In this form the lime is not available for liberating fixed ammonia during the short time that the liquor comes into contact with lime in the distiller. Frequently this inactive lime in the milk of lime may amount to 5 per cent, the active lime being defined as that portion of lime determined by the sucrose method. A large amount of overburned lime sometimes exists in the rejected "sand" from the lime slaker. Such overburned lime, when finely ground and added to the milk of lime, will become to a large extent available for reaction in the distiller.

(d) **Carbonated lime in the distiller.** When the temperature of the heater or the surface of contact between the steam and the liquor in the heater is insufficient, there is a considerable amount of carbon dioxide left in the heater liquor flowing into the prelimer and into the lime still. Even when the heater is working properly, a small amount of calcium carbonate is formed from this source. Lime that is carbonated is not available for liberating fixed ammonia under the conditions of distiller operation. True, a portion of the calcium carbonate found in the distiller waste comes from the unburned stone or air-slaked lime that is suspended in the milk of lime, but at least half of the quantity so found is due to carbonation by the carbon dioxide in the liquor. This loss may amount to fully 2 per cent of the total limestone under good operating conditions. It must be emphasized that the mud from the settling vats which contains high concentrations of carbon dioxide should be sent up to the very top of the heater so that all the carbon dioxide may be liberated before the liquor comes into contact with the milk of lime.

(e) **Excess lime in the distiller waste.** An excess of lime in the distiller waste is simply to insure complete liberation of fixed ammonia. The time of contact between the lime and the liquor in passing through the distiller is a matter of minutes, so that some excess of lime is necessary to facilitate the liberation of ammonia and its removal from solution. Any excess, however, more than 3 titer (or 4 grams of lime per liter) is unnecessary and represents just so much more available lime lost. At an excess of 4 grams CaO per liter with a volume of the distiller waste at 10 cubic meters per ton of ash, the loss is 6-8 per cent of the total good available lime, which is equivalent to about 10 per cent of the limestone charged in.

The total loss of available calcium carbonate in the limestone is therefore about 20 per cent. With a good grade of limestone containing 96 per cent calcium carbonate or better, the rate of consumption of raw limestone per ton of ash is calculated at 1.22 tons, which is confirmed in practice.

Salt.

Because brine is cheap the loss has not been a matter of grave concern to the manufacturer. Of course, any loss in handling is overshadowed by the magnitude of loss caused by the low average decomposition efficiency in the columns. By the very nature of the reaction, the loss of sodium chloride is more than 25 per cent, or the average decomposition is less than 75 per cent under good operating conditions. Hence a first requisite for the establishment of an ammonia soda plant is a cheap source of sodium chloride in the form of saturated brine. There are three main sources of loss of sodium chloride in ammonia soda plants:

(a) **Incomplete decomposition in the columns.** Under good operating conditions the decomposition of sodium chloride into sodium bicarbonate can average only 73 per cent, although as high an efficiency as 82 per cent for the reaction

$$NaCl + NH_4HCO_3 \rightarrow NaHCO_3 + NH_4Cl$$
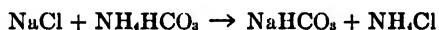
was attained, according to some laboratory investigations. If the mixed gases in the columns test low, if the concentrations of ammonia and sodium chloride in the ammoniated brine fall below normal figures, if the cooling surface in the columns is insufficient to get the desired draw temperature, the rate of decomposition falls still lower, and as much as 40 per cent of the total available sodium chloride in the ammoniated brine may be unconverted and discarded from the distillers. In addition, some sodium bicarbonate is dissolved by the wash water on the filters (2-3 per cent), so that the actual decomposition of sodium chloride into soda ash is still less.

(b) **Salt in the mud sent to the distiller.** As ammoniation of the brine is accompanied by purification, a considerable amount of semi-colloidal mud is formed by the treatment of the ammonia and carbon dioxide present. The precipitate should be completely settled in the vats, and the mud from the bottom of the vats disposed of by pumping to the distiller to recover the ammonia. The entire volume of the mud is saturated with sodium chloride and all the salt contained therein is lost. In order to minimize the loss of salt the mud must be pumped in as concentrated a form as possible. In order to prevent plugging of the vats by mud a slow moving scraper must be provided to keep the bottom of the vats open. Normally for sea salt the loss of salt through mud pumping is from 5 to 10 per cent when the sea salt brine has not been pretreated and purified. A further step in the economic use of salt is to pump the mud from the vats first into another settler, called the mud settler, where the mud is further concentrated and pumped from it to the distiller. It

is, of course, even more necessary to install a scraper or an agitator in this mud settler to prevent settling of the thick mud.

With a mud settler where all the mud from different settling vats is re-settled (and thus concentrated), it is possible to pump the mud continuously from the settler to the distiller at a concentration of not less than 95 per cent mud by volume. This is the volume of fine mud in a slimy form, measured in a 100-cc. measuring cylinder after 10 minutes of standing. The saving of good brine thus effected is indeed very considerable, especially where much mud is to be handled from the use of untreated sea salt in the absorber and vat system.

Besides the main losses mentioned above, there are many minor losses from the drippings of the pump packing glands, the leakage at the pipe joints, and so on, which are, however, insignificant in comparison to the others. The rate of consumption of salt per ton of soda ash made is thus 1.6-1.7 tons, which is the figure obtained in practice with a good grade of salt (brine).

The day is approaching when the utilization of salt in the process may be above 90 per cent. To this end an effort has been made to recirculate the mother liquor from the columns for the production of ammonium chloride crystals in conjunction with the manufacture of synthetic ammonia. A new modification of the ammonia soda process has been worked out, wherein the utilization of salt is 90-95 per cent (see Chapter XXVII, "Modifications and New Developments of Ammonia Soda Process").

Coal.

Coal in the soda plant may be used to generate electric current both for power and lighting, to calcine ammonia soda, and to generate steam for driving the carbon dioxide compressors, the filter and absorber exhausters, the air compressors, etc., the exhaust steam from which is utilized for ammonia distillation. For simplicity, the statement is based on coal, although oil or natural gas when available can be used to advantage in place of coal. If these larger units of machinery (generally located within the main engine room) are steam driven, the exhaust steam should be sufficient for the normal running of the distiller. If the filter liquor is excessively diluted and the volume to be distilled large, live steam may have to be added unless a bleeder turbine is installed. The sources of waste of steam leading to high consumption of coal are:

(a) **Excessive power consumed by the carbon dioxide compressors.** Because of weak kiln gas or weak furnace gas, or both, the piston displacement of carbon dioxide per ton of ash, *i.e.*, the r.p.m. of the compressors, may be excessive with a corresponding loss of steam and consequently coal. Even with the most simple gas delivery valves (and therefore low volumetric efficiency in the gas cylinders) there should not be more than 1400 cubic meters of piston displacement in the carbon dioxide compressor cylinders per ton of ash, unless the gas is abnormally weak in CO_2.

(b) **Excessive power consumed by the absorber exhauster.** If the absorber system is not air-tight, considerable air will leak in, not only giving an exhaust gas too low in carbon dioxide to be returned to the columns but also increasing the power required to draw the gas through the absorber exhauster. The piston displacement of the absorber exhauster per ton of ash should not be over 350 cubic meters at a vacuum of about 10 cm. Hg.

(c) **Live steam for distiller operation.** A greater loss, and a more serious one, in so far as regularity of operation and efficiency of the process are concerned, is the live steam required to supplement the exhaust steam in the distillers. The distiller foreman should avoid using live steam unless absolutely necessary, as, apart from the waste incurred from the use of additional steam, live steam is not as suitable for distillation as exhaust steam.

(d) **Steam leaks around the valves and piston rings.** The leakage of steam around Corliss valves is a serious matter. It causes high steam consumption and produces large quantities of exhaust steam. In worst cases such engines cannot run up to the rated speed due to high back pressure without having the throttle valve wide open with the governor set for the latest cut-off. The loss from this source depends upon the care and attention given to the repairs and maintenance of the steam cylinders.

(e) **Low fuel efficiency in the calcining furnace.** With poor bicarbonate crystals that cannot be filtered dry and that form scale in the furnace, furnace operation will be greatly handicapped and its capacity reduced. Consequently, the fuel required per ton of ash is increased. With the bicarbonate giving a 3-minute settling test, with efficient filters, and with a well-designed furnace running at full capacity, the fuel consumption should be about 1 ton of good coal for every 5 to 6 tons of ash calcined. The efficiency of the furnace is dependent upon its construction and the brick setting, but its capacity is also dependent upon the character of the bicarbonate crystals to be dried, *i.e.*, its crystalline character and moisture content. Hence efficiency in the tower operation is tied up with the fuel consumption in the furnace operation.

In general, in small plants the coal consumption is about 1 ton of coal per ton of ash. In large plants, considerably less than this figure (as low as 0.4 to 0.5 ton of coal per ton of ash) is obtained. This includes coal used for the generation of power and in the dryers. The low fuel and power consumption is another noticeable advancement made by the modern ammonia soda industry.

Coke.

As all the coke is used in burning limestone, the smaller the consumption of lime, the less the amount of coke required. But it also depends upon heat insulation and heat regeneration in the lime kilns and upon the grade of limestone burned, for a given rate of lime consumption. With a properly proportioned lime kiln and heavy fire-brick lining, *i.e.*,

with a tall kiln having a thick lining, the coke required should not be more than 1 ton to every 14 tons of normal stone. With a good distribution of coke in the charge and of air in the kiln, and with a good regenerating effect for heat both in the gas exit above and in the lime draw below, as low as 1 ton of coke to every 16 tons of normal stone has been obtained. This gives coke consumption at the rate of less than 0.10 ton per ton of soda ash made.

Sulfide.

A soluble sulfide, or $S^=$ ion, is a necessary constituent in the composition of ammoniated brine. This sulfide in contact with the cast-iron surface in alkaline solution forms a firm coating of ferrous sulfide on the internal walls of the apparatus and pipes, so that the sodium bicarbonate, and consequently the soda ash made, do not contain iron rust. When crude ammonia liquor is used, a large portion of the necessary sulfide is furnished by the crude liquor in the form of $(NH_4)_2S$ or NH_4HS. When the crude liquor does not contain enough sulfide, some Na_2S must be dissolved and added to the filter liquor for distillation. This is especially true when rock salt brine is used in which the magnesium content in the brine is low. Fused sodium sulfide (60 per cent, technically pure) can be used for this purpose. The amount of sulfide consumed per ton of ash depends largely upon the output of soda ash, upon the efficiency of the works, and upon the magnesium content in the brine. When ammonium sulfate is the only source of ammonia supply, all the sulfide required must be obtained from the sodium sulfide solution added to the feed liquor for

TABLE 148. Consumption of Raw Materials Per Ton of Soda Ash.

	Under Good Conditions	Under Average Conditions
Salt	1.50 tons	1.70–1.80 tons
Limestone	1.20 tons	1.30–1.50 tons
Coke at 7½% of the stone	0.095 ton	0.10–0.11 ton
Coal for boilers	0.25 ton	0.50–0.80 ton
Coal for dryers	0.16 ton	0.20–0.25 ton
Ammonia loss as $(NH_4)_2SO_4$	2–4 kg.	5.00–7.50 kg.
CO_2 gases (mixed gases to towers) piston displacement	1000 cu. m.	1100–1200 cu. m.
Ammoniated brine	5.7 cu. m.	6 cu. m.
Distiller waste	8.6 cu. m.	10 cu. m.

the distillers. A certain amount of sodium sulfide then must be dissolved and added to the filter liquor daily to replenish what is used in the system. The consumption of sulfide calculated to sodium sulfide per ton of soda ash is 0.001 to 0.002 ton when no crude liquor is available. When sea brine containing considerable magnesium salts is used, the sulfide consumption is considerably less than 0.1 ton per 100 tons of soda ash made.

A summary of the raw materials consumed is given here. Too much dependence cannot be placed on these figures, since a plant, owing to certain specially favorable conditions, may use one raw material more economically than another. Therefore a range is given in each case,

but even this range may be too narrow. One single factor that causes greater variation than any other is the size of the plant, *i.e..* the daily output of soda ash. A small plant will have a less favorable showing in the consumption of raw materials, no matter what effort is made to run it on an economical basis. The figures in Table 148 apply for the most part to large ammonia soda plants.

The whole ammonia soda process may be summed up by the following equation:

$$2NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$$
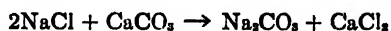
Of course, this reaction does not take place under ordinary conditions. Hence we have to introduce ammonia to bring about the ultimate result. The part that ammonia plays may be likened to a catalyst, but it is not strictly a catalytic action. A catalyst does not cause a change but simply hastens the reaction rate to the equilibrium point, whereas in this equation the reaction does not go and cannot be said to be hastened by a catalyst. From this equation, however, it is readily seen what relationship exists between the salt and the limestone required on the one hand and the soda ash and the calcium chloride produced on the other. The low conversion ratio, however, makes these figures run much higher, as seen from the foregoing discussion.

Chapter XXVII

Modifications and New Developments of Ammonia Soda Process

The ammonia soda process has proved its value for the past eighty years since the days of Solvay Brothers. It has reached a high state of perfection, but it must be said to have left something to be desired. In the first place, one of the essential raw materials—salt—used in the process is utilized only up to 73 per cent, and in small works the percentage conversion is still less. This leaves about 30 per cent overall of salt taken into the process unconverted into sodium bicarbonate, and all this salt is practically wasted. This is caused by the nature of the reaction; for, unless the waste liquor containing the unconverted salt can be used over again in the process, or unless effort is made to recover the salt from the liquor, little can be done to improve the situation. In certain plants such salt has been recovered and turned into refined salt, but the amount is very small. As a consequence, the existence of the ammonia soda industry presupposes a cheap source of salt and plenty of it. preferably in the form of saturated brine. No country which has an expensive salt supply, or whose salt bears a high tax under the government control, can afford to use the salt for the ammonia soda industry without certain special concessions from the government for tax exemption.

In the second place, ammonium chloride formed in solution after the reaction cannot be readily utilized. The common practice is to subject the liquor to distillation with lime in order to free the ammonia and use it over again in the process. The ammonium chloride in the liquor, although in a useful form, cannot be available for commercial purposes without a special treatment. Many processes have been proposed to obtain ammonium chloride as crystals, and numerous patents have been taken out in regard to the recovery of ammonium chloride in a solid crystalline form from the liquor. Among these may be mentioned those proposing to concentrate the liquor and cause ammonium chloride to crystallize at a low temperature by dissolving in the liquor, salt, sodium nitrate or other sodium salt. The operation is costly and the ammonium chloride liquor is difficult to handle on account of its corrosive properties when it is hot and concentrated. Such a process has from time to time been the subject of patents by the I. G. Farbenindustrie, A. G. in Germany, the Brunner, Mond & Co., in England (now Imperial Chemical Industries, Ltd.) and the Solvay Process Co., in America (now in Allied Chemical and Dye Corp.). We shall not attempt to dwell on this phase

of development at any length, but prefer to refer those interested to the patent literature, because such processes have not been used extensively.

One important modification which is being developed into a new process, and which was not originally intended to be a part of the ammonia soda process, was due to the pioneering work of Prof. W. Gluud and Dr. B. Loepmann when they were working in the Gesellschaft fuer Kohlentechnik Laboratories at Dorstfeld near Dortmund, Germany, as early as 1924. Much of the process is not new, however, for the use of solid ammonium bicarbonate for the precipitation of sodium bicarbonate from brine was mentioned by H. Schreib [1] as early as the beginning of this century. The important feature in this process is the introduction into the solution of a soluble salt called the "Intermediate Salt" having Na^+ as cation and as anion any radical other than Cl^-. The regulation of the concentrations of various ions in solution for the precipitation of ammonium chloride and sodium bicarbonate crystals from the liquor, and the manipulation of the operations are rather ingenious, and deserve discussion at some length. The Institute at Dorstfeld was engaged in researches on coal products, carbon dioxide, ammonia and the by-products of the coal and coke industry. Heretofore, ammonia was all converted to ammonium sulfate as fertilizer by means of free sulfuric acid, which after all has no value as an ingredient in the fertilizer. Besides, the useful sulfuric acid is rendered unavailable, and in certain cases the sulfate part of the fertilizer may have some harmful effect on the soil. Consequently, to save this valuable sulfuric acid, the I. G. Farbenindustrie, A. G. developed a process of fixing ammonia by means of finely pulverized gypsum (calcium sulfate) suspended in ammonia solution, by carbonation with carbon dioxide gas. This is the Gypsum Process. This successful process marks a distinct improvement in the manufacture of ammonium sulfate as fertilizer dispensing with sulfuric acid. These German investigators in the Kohlentechnik Institute were attempting to fix ammonia in the form of some other salt than the sulfate, possibly as the chloride, as ammonium chloride had been reported by Prof. Bosch, Prof. Wagner and others to possess as favorable fertilizer properties as ammonium sulfate for many crops. A natural course for these investigators to follow would be first to convert the free ammonia obtained from coke manufacture to ammonium bicarbonate by the waste CO_2 gas, and then to convert the bicarbonate to the chloride by displacing the bicarbonate ion. It would also be natural to utilize the chlorine from common salt for this purpose by removing the bicarbonate ion with sodium as sodium bicarbonate, as in the Solvay Process. Now, it was an easy matter to precipitate the bicarbonate as sodium bicarbonate, but how was it possible to precipitate the highly soluble ammonium chloride by a less soluble sodium chloride? Here, an ingenious device was worked out by the use of an Intermediate Salt to obtain a condition of equilibrium relative to the solubility products involving Na^+, NH_4^+, Cl^- and other ions

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[1] Schreib, "Die Fabrikation der Soda nach dem Ammoniak-Verfahren."

in the liquor (see below) and to introduce NaCl in a finely divided state. This caused separation of ammonium chloride from solution, thereby fixing it as chloride. This ingenious device was looked upon as a successful attempt to fix ammonia as ammonium chloride in place of ammonium sulfate. But in order to achieve this, the bicarbonate must first be removed as sodium bicarbonate, a rather soluble acid salt of sodium, but very much less soluble in the presence of high concentrations of other salts in solution. For example:

> In water at 30° C., solubility of $NaHCO_3$ is .... 11.02 g/100 cc.
> In 11% brine solubility of $NaHCO_3$ is about .... 4.7 g/100 cc.
> In 20% brine solubility of $NaHCO_3$ is .... 2.2 g/100 cc.
> and in saturated brine solubility of $NaHCO_3$ is .... 1.3 g/100 cc.

Soon it was pointed out that this by-product of sodium bicarbonate should have a great commercial value as a source of soda. Attention was then directed to working it up in the form of caustic soda or soda ash. With the successful attempts, especially in converting the sodium bicarbonate to caustic soda directly, the situation has changed considerably; and it was gradually pointed out that this was another form of the soda process, a modification of the Solvay Process, whereby solid ammonium chloride is produced in conjunction with sodium bicarbonate, making ammonium chloride and soda ash or caustic soda joint products. Great significance, however, is attached to the fact that in fixing the free ammonia as ammonium chloride, it brings the two branches of fundamental heavy chemical industry—the Solvay Process and the synthetic ammonia industry—more closely together; in fact the two may now exist side by side in one grouping. For the fixed nitrogen industry requires some means of fixing free ammonia as a nitrogenous fertilizer, and this is one way of fixing it for fertilizer purposes, and for other uses as well. Further, in the fixed nitrogen industry, in obtaining hydrogen from semi-water gas or coal gas, there is a great excess of carbon dioxide gas which is released to the atmosphere. This waste CO_2 gas now may be used for the production of ammonium bicarbonate as an intermediate step in the manufacture of soda and ammonium chloride by this process.

The operations involved in the production of ammonium bicarbonate crystals are to pass carbon dioxide gas into ammonia solution containing approximately 20 per cent NH_3 by weight, first in saturating and then in precipitating towers, in the same way as in the Solvay Process. The crystals of ammonium bicarbonate are filtered off from the slurry in centrifugals or on rotary vacuum filters, as for ammonia soda. The filter liquor is sent through the absorber for the absorption of further ammonia, and the solution is cooled and pumped to the carbonating towers arranged in much the same way as in the Solvay Process. Ammonium bicarbonate crystals so obtained are used to precipitate sodium bicarbonate crystals in a number of precipitation tanks, each provided with a high-speed stirrer.

In fact, many Solvay works have been making ammonium bicarbonate

this way for years; but because of the limited field for the use of ammonium bicarbonate in quantities, it has not been made on a scale comparable with that of sodium bicarbonate. Now, with the use of ammonium bicarbonate as the intermediate product in fixing ammonia as ammonium chloride, this field will be greatly extended as never before.

In this connection, by way of digression, it may be mentioned that a process has been worked out for obtaining crystals of ammonium bicarbonate that have such a low vapor pressure that they may be packed in gunny bags and kept in storage for months without any material loss. This is accomplished by coating or cementing the crystals with mineral oil, sugar or other inert materials.* This will remove many objections to the use of ammonium bicarbonate commercially because of its unstable character and the necessity of special air-tight containers.

So far only the batch process for the precipitation of sodium bicarbonate has been in use, but it is not altogether impossible to develop this step further into a continuous process, such as in the other steps of the operation. The development at the present stage is limited to a comparatively small capacity on account of the batch character at this particular stage.

Quite different from the Solvay Process is the fact that this process starts with a solution virtually saturated with respect to both NaCl and NH_4Cl. For some time in the beginning of the development, the difficulty had come from the fact that ammonium chloride and sodium bicarbonate would precipitate together when ammonium bicarbonate was introduced into such a concentrated solution of sodium chloride and ammonium chloride. Many attempts had been made in the beginning to separate ammonium chloride from sodium bicarbonate in the precipitate, by resorting to the use of strong ammonia solution (40 per cent NH_3) for dissolving out ammonium chloride in the form of a highly soluble ammonia complex such as $NH_4Cl \cdot 4NH_3$. This involved the use of a very strong ammonia solution, the handling of which caused considerable difficulties, and the loss of ammonia placed a serious handicap on its development.

Finally, the use of strong ammonia solution was dispensed with, and the difficulty was solved by dividing the operation into two steps: first the precipitation of sodium bicarbonate, and then the precipitation of ammonium chloride in separate vessels at different temperatures by carefully regulating the concentration of various ions in the solution so that only one precipitates at a time.

The principle underlying this process is to obtain a saturated solution containing NH_4^+, Na^+, Cl^-, and another ion (A^-). This we may express as NH_4Cl, NaCl and NaA in solution, the NaA being the intermediate salt present in quantities substantially equivalent to the amount of $NaHCO_3$ to be precipitated from the solution. The balance of Na^+ may be considered to exist as $Na^+ Cl^-$. At the same time, NH_4Cl may be said also to be present to saturation under these conditions. When to this

* D.R.P.—622,876; D.R.P.—485,054; etc:

solution are added ammonium bicarbonate crystals, NH_4HCO_3 dissolves and gradually displaces sodium bicarbonate as precipitate. Thus,

$$Na^+A^- + NH_4^+HCO_3^- \rightarrow NaHCO_3 \downarrow + NH_4^+A^-$$

However, the concentration of the NH_4^+ ions in solution has been so regulated that, when $NaHCO_3$ is thrown down by NH_4HCO_3, the additional quantity of NH_4^+ ions formed, together with NH_4^+ ions already present in solution, does not exceed the solubility product of NH_4Cl with the concentration of Cl ions present in solution at the temperature in question (*e.g.*, 35° C.), so that no NH_4Cl separates out with $NaHCO_3$. But as much of Na^+A^- as is equivalent to the NH_4HCO_3 added has been converted to NH_4A in solution. This increases the NH_4^+ concentration in solution by the amount equivalent to the ammonium bicarbonate added. When, therefore, the solution after filtration is cooled to say 10 to 15° C. below the temperature of the sodium bicarbonate precipitation (*e.g.*, 20-25° C.), and common salt is introduced, the salt dissolves and in its solution furnishes additional Cl^- ions which, together with the Cl^- ions already present and with the increased concentration of NH_4^+ mentioned above, now cause the solubility product of NH_4Cl to be exceeded, and NH_4Cl begins to precipitate. This takes place in a separate precipitation tank.

Let $C_{NH_4^+}$ = concentration of NH_4^+ ions originally present as NH_4Cl in solution.

$\quad\quad C_{Cl^-}$ = concentration of total Cl^- ions originally present as NH_4Cl and $NaCl$ in solution.

$\quad\quad C_{Na^+}$ = concentration of total Na^+ ions originally present as $NaCl$ and NaA (intermediate salt) in solution.

$\quad C_{HCO_3^-}$ = concentration of HCO_3^- ions.

$\quad C'_{NH_4^+}$ = increase in concentration of NH_4^+ ions by the addition of NH_4HCO_3.

$\quad\quad C'_{Cl^-}$ = increase in concentration of Cl^- ions by the addition of $NaCl$.

$\quad\quad S_{NH_4Cl}$ = solubility product of NH_4Cl.

$\quad S_{NaHCO_3}$ = solubility product of $NaHCO_3$.

Then $(C_{NH_4^+} + C'_{NH_4^+}) \times C_{Cl^-} < S_{NH_4Cl}$ at 35° C.;

While $C_{Na^+} \times C_{HCO_3^-} > S_{NaHCO_3}$ at 35° C.

However, when the solution is cooled and salt introduced, additional Cl^- ions are formed, $NaCl \rightarrow Na^+ + Cl^-$.

Then $(C_{NH_4^+} + C'_{NH_4^+}) \times (C_{Cl^-} + C'_{Cl^-}) > S_{NH_4Cl}$ at 15° C.

Then and only then will ammonium chloride precipitate. Further, it can be seen that by the displacement of ammonium chloride from solution with an amount of $NaCl$ equivalent to the amount of ammonium bicarbonate previously added to the solution for the precipitation of $NaHCO_3$, .the original concentrations of the various ions present in the solution prior to the sodium bicarbonate precipitation are restored, so that the treatment of the liquor (after filtration) with ammonium bicarbonate may be repeated and the cycle of operations started anew, and so on indefinitely. Also, the volume of the filtrate is substantially the same as

that of the original solution, unless too much wash water has been added or unless too much mother liquor has been removed with the sodium bicarbonate or ammonium chloride crystals filtered off. This increment of Cl⁻ ion concentration, coupled with cooling, is all that is necessary for the precipitation of NH_4Cl. But it is apparent that the presence of too much of the so-called intermediate salt (NaA) is undesirable, because of the depletion of Cl⁻ ions, causing difficulties in the precipitation of NH_4Cl and because of the presence of high intermediate salt and sodium chloride in the ammonium chloride crystals formed, although it makes little difference as far as the sodium bicarbonate precipitation is concerned. On the other hand, if too little intermediate salt (NaA) is used, assuming that the solution is still saturated with respect to both NaCl and NH_4Cl under these conditions, the preponderating amounts of NH_4Cl will suppress the equilibrium of the following reaction, causing the reaction to be less complete:

$$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$$
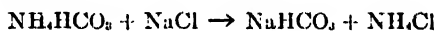
or ultimately causing NH_4Cl to separate together with $NaHCO_3$, contaminating the sodium bicarbonate obtained. Hence there is an optimum range in which the intermediate salt should be present for the reaction to take place in the presence of both NaCl and NH_4Cl at high concentrations, if pure products are to be obtained. This concentration of the intermediate salt is generally from 6 to 10 per cent by weight, depending on the character of the negative ion and its equivalent weight. Precipitation of sodium bicarbonate or ammonium chloride may be said to be due to this quantity of the intermediate salt present, which first assumes the form of an ammonium salt and then of the corresponding sodium salt. The whole situation may be summarized thus: In sodium bicarbonate precipitation the reaction takes place virtually as follows:

$$NaA + NH_4HCO_3 \rightarrow NaHCO_3 \downarrow + NH_4A$$
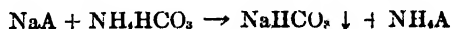
whereas in ammonium chloride precipitation, essentially the following reaction occurs:

$$NH_4A + NaCl \rightarrow NH_4Cl \downarrow + NaA;$$
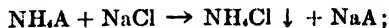
thus the condition is restored and the cycle may be repeated indefinitely. In this way, the intermediate salt acts as a buffer for the exchange, oscillating between the ammonium and sodium salt as the cycle is repeated.

Such is the role that the intermediate salt plays in this ingenious combination. It can be seen that the anion A⁻ may be anything other than the Cl⁻ ion, provided that its sodium and ammonium salts are sufficiently soluble, and provided that the anion of the intermediate salt does not form an insoluble salt with calcium, magnesium, barium, iron, etc. which may be present as impurities in the crude salt used. In practice sodium nitrate ($NaNO_3$), sodium sulfocyanate (NaCNS), sodium sulfate (Na_2SO_4), etc., or their corresponding ammonium salts have been used; any one of these may serve the purpose equally well, apart from certain

practical difficulties attending the operation, and from their economic considerations. Sodium or ammonium phosphate cannot be used because it would be precipitated by calcium, magnesium, etc. in the crude salt used, thereby causing loss of the phosphate; and sulfate cannot be used when the crude salt contains much barium chloride as impurity. Other conditions being equal, the lower the equivalent weight of the intermediate salt, the better. If the anion of the intermediate salt is Cl⁻, then the process is nothing more nor less than the normal Solvay Process, in which case, with the simultaneous presence of large NH_4Cl and $NaCl$ in the liquor, decomposition of $NaCl$ by NH_4HCO_3 would be greatly impeded, as mentioned above.

For the process to work successfully, it is necessary also to have as large a difference (or interval) as possible between the temperature at which sodium bicarbonate is precipitated and that at which ammonium chloride is precipitated. Too small a temperature interval would cause difficulties in getting the two products, ammonium chloride and sodium bicarbonate, separated out individually, thus contaminating sodium bicarbonate with ammonium chloride, and *vice versa*. On the other hand, there are practical difficulties in trying to make the temperature interval as large as might be desired. For, if the temperature of the $NaHCO_3$ precipitation is raised too high, say above 40° C., decomposition of $NaCl$ would be less complete because of the increased solubility of $NaHCO_3$ at the higher temperature. Moreover, the decomposition of NH_4HCO_3 to CO_2 and NH_3 would be excessive, and the loss of NH_3 in the reaction, as well as that due to exposure of the warm liquor to the air, would be greatly increased. On the contrary, if we set the precipitation temperature of NH_4Cl too low, say much below 20° C., we are confronted with difficulties in cooling the liquor with the temperature of the cooling water generally available, unless refrigeration is employed. As a rule, the crystal formation at a low temperature is poorer, although the solubility of the crystals is much less, the efficiency of conversion better, and the loss less. In plant operation, the temperatures for the precipitation of sodium bicarbonate and ammonium chloride are 40 and 25° C., or 35 and 20° C., or 30 and 20° C., respectively. For example, for laboratory test, take 5 liters of 8 per cent Na_2SO_4 solution and saturate it with table salt at room temperature by stirring into it about 1600 g of $NaCl$. Bring the temperature to 40° C., and filter off any undissolved solids. Add to the solution 125 g of NH_4HCO_3 (air-dried crystals) per liter of the solution in small portions very slowly; keep stirring and filter off the precipitate of $NaHCO_3$. Thoroughly wash the sodium bicarbonate crystals on the filter. Cool the filtrate to 20° C. and introduce finely pulverized table salt (-40 mesh or finer) to the filtrate in the ratio of 85 g of salt per liter of solution, and keep the agitator constantly working. The precipitate of NH_4Cl * is centrifuged off and washed with a small amount

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* In the first few cycles, little ammonium chloride would separate because the solution is not yet saturated with this salt.

of water. This filtrate is now heated to 40° C. again for sodium bicarbonate precipitation, as before. The cycle may be repeated an indefinite number of times, it being essential to filter the cake dry, returning all mother liquor to the filtrate; to regulate the concentrations of various ions in the liquor; and to keep the volume of the mother liquor at each operation constant, replenishing the loss of mother liquor with a little strong wash liquor each time. A little intermediate salt is also added from time to time to replenish its loss in the cycle.

In practice, there are a great many "kinks" attending the operations which can be appreciated and guarded against only by those of long experience in the working of the process. For instance, if one does not regulate the relative concentrations of different ions in the liquor, one may get very impure or unsalable products. If one has not used proper quantities of ammonium bicarbonate or salt per cu. m. of liquor, one may soon find the relative concentrations in the resulting liquor out of the range, thereby permanently impairing the solution for subsequent opertions; and this could not be restored without special treatment. If for some reason the crystals obtained are too fine, and cannot be filtered dry, much liquor would be entrained in the cake, and the inclusion of much mother liquor in the cake may contaminate the product with many impurities from the highly concentrated liquor, or may affect the relative concentrations of certain ions in the resulting liquor because of loss of volume of the liquor. Consequently, either the concentration of the liquor could not be maintained, or the volume thereof could not be kept constant, or the wash water would be left on hand in disproportionate quantities, or the loss of the intermediate salt, or ammonia, or both, would be excessive. Such conditions may spell failure for the undertaking, just as much as in the early days in the history of the ammonia soda process before Solvay's time. Again, the presence of $NaHCO_3$ in NH_4Cl (or $NaCl$ in NH_4Cl) may be caused by low Na^+ ion concentration during the previous precipitation of $NaHCO_3$, or by complete absence of magnesium salts in the crude salt used; this may be avoided by having proper concentration of free ammonia in the bicarbonate mother liquor before the addition of $NaCl$ for the precipitation of NH_4Cl (see below).* With good experience, it is possible to follow the progress of the reaction by inspecting the color change of the solution or by observing the change in the specific gravity of the liquor. The pH values change somewhat, but this is not a good index because of very strong buffer action and salt effect in the liquor.

The key to success lies in so regulating the temperature, concentration and operating conditions that reasonably coarse crystals are obtained in order that the resulting sodium bicarbonate may be filtered dry and free from impurities. This returns the mother liquor to the system and keeps

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* This free ammonia concentration should have a certain definite value for proper precipitation of ammonium chloride, while the extent of bicarbonation by passing CO_2 gas into the liquor during sodium bicarbonate precipitation varies according to whether the precipitation is carried out in open vessels or under considerable pressure.

its concentration within the orbit for the subsequent cycles. It is found also that coarse ammonium bicarbonate crystals are conducive to the formation of coarser sodium bicarbonate crystals because of crystallographic isomorphism between the two. Also, slower rate of addition of ammonium bicarbonate crystals to the solution causes the formation of coarser sodium bicarbonate crystals, presumably because of the smaller number of nuclei on which crystals may grow. For, upon the addition of a small portion of ammonium bicarbonate crystals, it may be observed that at first they are dissolved and the solution remains clear. Here the temperature decreases to a definite point, P (Fig. 121). Gradually, how-
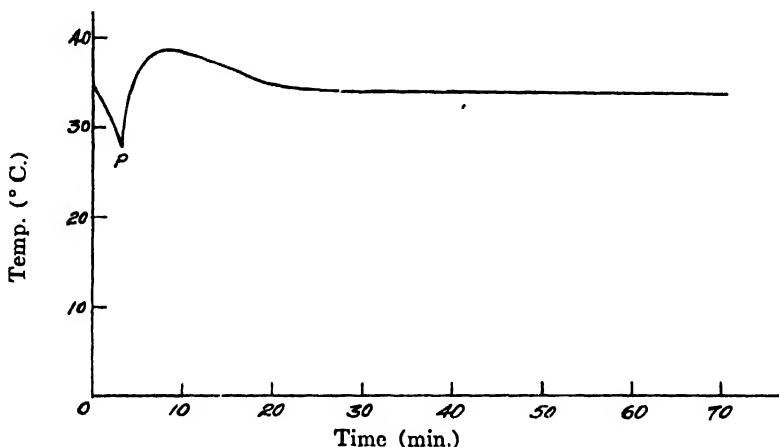
Fig. 121. Change of temperature during the addition of NH_4HCO_3 to $NaHCO_3$ precipitator.

ever, upon the addition of further quantities. the solution becomes cloudy. the crystals appear, and the temperature starts to rise to a maximum. When further quantities of ammonium bicarbonate are added, the crystals grow coarser and settle more rapidly, and the temperature falls slowly and gradually until the last portion of ammonium bicarbonate has been added. Under such conditions, the sodium bicarbonate crystals are more easily filtered and are filtered drier. All such details cannot be entered into here, but suffice it to say that they have important bearing on the purity of the products obtained and on the successful operation of the process.

Under average operating conditions the sodium bicarbonate obtained should have (on dry basis) the composition as shown in Table 149.

TABLE 149. Composition of Sodium Bicarbonate.

1.	NaCl	1 per cent or less
2.	NH_4HCO_3	3-4 per cent (which is recovered upon calcination)
3.	Intermediate salt	a small fraction of 1 per cent
4.	$NaHCO_3$	96 per cent
5.	Free moisture	15-18 per cent H_2O when rotary vacuum filter is used
6.	Decomposition of NaCl	91 per cent on the basis of NH_4HCO_3 used;

and the ammonium chloride obtained should have (on dry basis) the composition as shown in Table 150.

TABLE 150. Composition of Ammonium Chloride.

1.	NaCl	1-2 per cent
2.	NaHCO₃	A small fraction of 1 per cent
3.	Intermediate salt	A small fraction of 1 per cent
4.	NH₄Cl	96-98 per cent
5.	Free moisture	3-5 per cent when centrifuge is used
6.	Yield of NH₄Cl	93-94 per cent on the basis of NaCl used.

The purity of NH_4Cl depends greatly upon the purity of salt used. Practically all the impurities in the salt, such as Ca^{++}, Mg^{++}, etc., precipitate as $CaCO_3$, $MgCO_3$, etc., together with NH_4Cl. In order to avoid contamination of NH_4Cl, a good grade of salt should be used, or purification of brine for the winning of a high-grade table salt is recommended. As far as the operation is concerned, it is only possible to minimize the contamination of NH_4Cl from such a source. Ammoniation (as mentioned above) of the liquor before the addition of salt is very useful. This converts $NaHCO_3$ held in solution at a higher temperature into normal sodium carbonate, which will remain in solution upon cooling the liquor for ammonium chloride precipitation. Further, this free ammonia present to the extent of only 0.3 per cent NH_3 or less is found to have also the tendency to hold in solution calcium and magnesium impurities in the salt, so that to a large extent the impurities will not separate out with the ammonium chloride precipitate. This may be explained by assuming the formation of some double salt of calcium and magnesium carbonates which separates out only slowly, and which will not separate in time with NH_4Cl crystals, or, if separated at all, will exist in small particles which may pass through the screen when the NH_4Cl slurry is centrifuged. Thus, a purer ammonium chloride is obtained from salt containing a small amount of Mg salts as impurities (.3 per cent as $MgCO_3$), than otherwise from salt which contains no magnesium salts. For it was found that without this small quantity of Mg salts in the salt, the ammonium chloride obtained may contain high sodium bicarbonate, sometimes as high as 7 per cent $NaHCO_3$.[*] The double salt formation then slowly separates out in the settler provided for this purpose, thus eliminating from the ammonium chloride crystals most of the impurities in the salt used. On the other hand, if the ammonia concentration is too high, calcium and magnesium compounds will separate rapidly from the solution together with the ammonium chloride crystals, thus causing all the calcium and magnesium in the salt to separate with the ammonium chloride.

The presence in the liquor of free ammonia or ammonium hydroxide requires that it be again neutralized with CO_2. This is done by introducing CO_2 into the sodium bicarbonate precipitation vessel (precipitator) after the addition of the last portion of NH_4HCO_3. The pressure of CO_2

[*] See **Loepmann**, "Berichte der Gesellschaft fuer Kohlentechnik," pp. **78-81**, Band IV, Heft 1, 1931.

gas of about $\frac{1}{2}$ atmosphere (gauge) above the liquor is sufficient for this purpose. This is in line with the Solvay operation, but CO_2 is introduced here for three purposes:

(1) The bubbling of CO_2 gas into the solution converts more of the CO_3^{--} ions back into HCO_3^- ions and further furnishes excess CO_2 to push the equilibrium of reaction toward completion in the conversion of $NaCl$ to $NaHCO_3$ by the mass action principle;

(2) This helps maintain the temperature of reaction by the heat liberated by neutralization of ammonia by CO_2 in order to secure good crystal formation, and also serves to stir the solution; and

(3) As the liquor has a tendency, in the course of the operation, to contain more and more free ammonia (shown by its rising alkalinity) as the result of decomposition of NH_4HCO_3 and liberation of CO_2 gas from the liquor, bubbling of CO_2 gas here will counteract such a tendency.

In practice, about 10 per cent of CO_2 required is passed in this way. The heat of neutralization utilized in this way is desirable, inasmuch as the heat effect in the precipitation of $NaHCO_3$ by NH_4HCO_3 is negative, *i.e.*, the reaction is endothermic. This can be understood from the fact that the heat of solution of NH_4HCO_3 is -6.69 kg. Cal. per mol in a large quantity of water, while the heat of solution of $NaHCO_3$ is only -4.30 kg. Cal. per mol. In fact, during the precipitation of $NaHCO_3$ the solution would be cooled about $3°$ C. but for the heat generated by neutralization.

In this connection it may be added here that the heat effect in the precipitation of NH_4Cl by $NaCl$ is just the reverse, *i.e.*, the reaction is exothermic, and there is a rise in the temperature of the liquor when salt is being added; *e.g.*, the heat of solution of $NaCl$ per mol in 200 mols of water is 1.28 kg. Cal. as against that of NH_4Cl of 3.89 kg. Cal. per mol in the same amount of water. In practice, a rise of temperature of more than $2°$ C. is observed. Therefore, to keep the temperature down it is necessary to pass cooling water at a good rate during ammonium chloride precipitation.

Losses and consumption of raw materials in this process are comparable with those in the Solvay Process. The process is handicapped in that the precipitation operations of both $NaHCO_3$ and NH_4Cl are not yet continuous, and larger plants beyond one hundred tons of soda ash per day have not been practicable without multiplying the number of units greatly. Table 151 shows losses and consumption of raw materials in this process under average operating conditions.

TABLE 151. Consumption of Raw Materials.

1. Salt	1.23 tons per ton of soda ash made	
2. Limestone	1.25 " " " " " " "	
3. Intermediate salt	10 kg. " " " " " "	
4. Loss of ammonia	3-4 kg. as $(NH_4)_2SO_4$ per ton of soda ash made.	

The purities of the main products are:

1. Sodium bicarbonate 99.2% NaHCO$_3$
2. Soda ash 99.1% Na$_2$CO$_3$
3. Ammonium chloride 96-98% NH$_4$Cl depending on the quality of crude salt used.

The other items of consumption, such as steam, electric power, etc., are also not essentially different, although the ammonia loss may be somewhat higher because of smaller scale of operation. The quantities of cooling water required may be greater because of relatively insufficient cooling in the NH$_4$Cl precipitators. Nowadays, the plant working on this process is also conducted in a closed system throughout, and various ammonia gas washers and scrubbers are in use.

Centrifuges of different types have been used to a great extent because more complete separation of mother liquor from the crystals is essential (see below).

The consumption of salt given above is indeed very favorable, and shows considerable saving as compared to 70-73 per cent conversion with 1.70-1.80 tons of salt consumed per ton of soda in the Solvay process. In fact, it is possible to obtain average conversion efficiency in this process as high as 95 per cent. This is an advantageous feature, and is of great value to a country where salt supply is particularly expensive. Against this must be mentioned that, whereas in the Solvay process natural brine is used, in this process only solid salt can be used, which adds considerable cost to the working up of brine for the dry salt crystals. Further, salt used in this process must be pulverized to minus 40 mesh or thereabouts, and the power required is also an item in its cost. But the fact that its conversion efficiency is high, coupled with the fact that soda here is obtained as a by-product—if we view this process as a means of fixing free ammonia as ammonium chloride for fertilizer—makes this process very interesting. It may also be pointed out that, whereas this process requires as raw material ammonium bicarbonate crystals which necessitate additional equipment and cost in their manufacture, the practice in the Solvay process is just to pass CO$_2$ gas into ammoniacal brine, forming NH$_4$HCO$_3$ *in situ,* thus greatly simplifying the operation. However, the sulfuric acid saved, which otherwise would have to be employed in fixing the free ammonia as ammonium sulfate, of which the sulfate part is only a sort of vehicle and has no value whatsoever as a fertilizer, will considerably outweigh all such considerations and justify its adoption in conjunction with the fixed nitrogen industry (synthetic ammonia industry), where ammonium chloride can be sold as fertilizer. Here the happy combination exists, and here the nitrogen industry with its large supply of waste CO$_2$ gas, or the gas and coke industry with its by-product crude ammonia liquor, can join hands with the soda industry, particularly where salt is too expensive for the establishment of a regular Solvay plant. The sodium bicarbonate here is generally converted to caustic soda by wet "calcination" with steam, so that calcining in rotary soda dryers to soda ash is eliminated, and furthermore caustic and mud from the causti-

cization process mȧy be utilized in the preparation of "ammonia lime" (see below).

Again, from the comparison of this process with the Solvay process, it is an undeniable fact that the sodium bicarbonate crystals are likely not to be so large as those from the Solvay process, because of lack of countercurrent character and lack of temperature gradient in such precipitators; but with good regulation it is possible to obtain fairly satisfactory crystals that may be filtered reasonably dry, washed well and calcined in rotary furnaces without difficulty, where soda ash is desired. Under good operating conditions, the size of the crystals of sodium bicarbonate from the Solvay process may be as large as 0.10-0.20 mm., whereas the size of the crystals of sodium bicarbonate by this process is generally from 0.05 to 0.10 mm. Also, as the solution is so concentrated (specific gravity 1.21-1.23, depending upon the quantity and nature of intermediate salt used), *i.e.*, as the liquor is so "heavily loaded" with soluble salts, the product from such a liquor is likely to be contaminated with salts from the mother liquor included in the crystals. Here, centrifuges serve well; either the automatic type, or the strictly continuous type, with rubber-coated baskets and screen, or made of Stainless steel material, such as KA_2SMo, has been found very advantageous for large-scale production, as these centrifuges retain the minimum amount of mother liquor in the crystals. But where rotary vacuum filters are used, as in the filtration of sodium bicarbonate, the best arrangement is to have "double filtration," *i.e.*, two filters installed in series, the cake from the first filter being suspended in a wash liquor, using a screw mixer. The suspension is then refiltered on a second rotary filter, while fresh water is used for washing the cake on the second filter, as shown diagrammatically in Fig. 122. These filters are so designed as to be able to separate the wash water from the filtrate (mother liquor). In this way, sodium bicarbonate containing only 0.10-.015 per cent NaCl has been obtained.

One particular application of this process (as was mentioned above) is in connection with working the sodium bicarbonate so obtained directly into caustic soda. This is done by directly converting the bicarbonate into carbonate liquor used directly for causticization. Here, smaller crystals of sodium bicarbonate are of no consequence. For this purpose, crude sodium bicarbonate from the filters is added to hot water or condensate to form a suspension, and is pumped into the top of a column somewhat like a small distiller, while steam at moderate pressure (about 20-50 lbs. gauge) is passed in at the bottom. This decomposes sodium bicarbonate suspension into a perfect solution of soda ash and some sesquicarbonate, and the hot liquor is directly sent to the causticizer. This is an application of "Wet Calcination" (see Chapter XXI). A well-insulated tank must be used for the storage of the hot liquor to prevent crystallization of Na_2CO_3, or freezing. (For further details, see also Chapter XIX on the manufacture of caustic soda by the lime process.)

$$2NaHCO_3 + heat \rightarrow Na_2CO_3 + CO_2 + H_2O$$
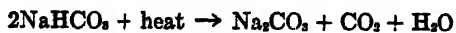
The saving in the heat (steam) here is considerable, while the CO_2 gas, after passing through the condenser, is available for carbonation in a very rich form. It is likely that a little more lime is required, because of
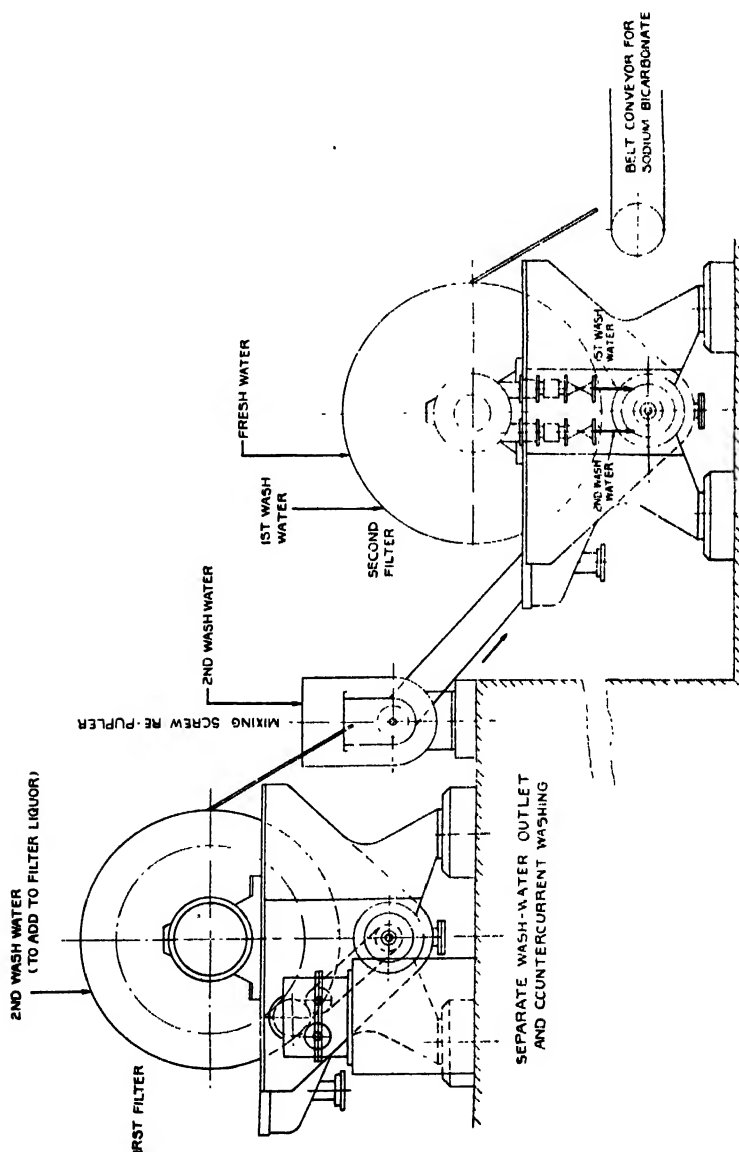
FIG. 122. Double filtration method for filtrate containing high soluble salts that would cause considerable impurities in filter cake.

incomplete decomposition of sodium bicarbonate. The causticized liquor may then be concentrated for the manufacture of liquid or solid caustic, as usual.

A word may be said of ammonium chloride as a fertilizer. It has been definitely established that its fertilizer properties are in many cases as effective as those of ammonium sulfate, barring only certain plants, such as tobacco, citrous fruits and certain starch-forming plants which cannot tolerate much chlorine in the soil. While, in general, excess chlorine is harmful to many plants, small amounts seem to be beneficial in protecting them from excessive drying in drought periods. The relationship of the chlorine content in tobacco leaf to its fire-holding capacity has been established, a high-chlorine tobacco leaf possessing poor fire-holding ability.

For crops in general, ammonium chloride has been found to have good fertilizing properties. Like ammonium sulfate, it renders the soil acid, but when ammonium chloride is used, acidity in the soil may be washed away more readily than is the case with ammonium sulfate. It may be mixed advantageously with an alkaline fertilizer such as sodium nitrate, calcium nitrate or calcium cyanamide, or with pulverized limestone or dry caustic mud. Its relation to ammonium sulfate is the same as that of potassium chloride to potassium sulfate, and so it is generally used as an ingredient in mixed fertilizers. In the mixed fertilizer, such as 4-8-8 or 6-8-4, ammonium chloride serves as the source of nitrogen just as well as ammonium sulfate, the only difference being that when ammonium chloride is used for this purpose as the source of potash, potassium sulfate rather than potassium chloride should be used. It is seldom that ammonium chloride is used alone, *i.e.*, unmixed with the other ingredient, but for many crops and soils, NH_4Cl may be freely substituted for $(NH_4)_2SO_4$ as a nitrogenous fertilizer; the reason that it has so far not been so used extensively is due to the present high cost of this material.

Ammonium chloride is more concentrated and contains a higher percentage of nitrogen than ammonium sulfate; consequently limestone or precipitated calcium carbonate sludge from the caustic soda manufacture is frequently mixed with it so that it will contain about 16 per cent NH_3 and 22 per cent CO_2. This is sold under the name of "Ammonia Lime" (Ammonkalk), about 50 per cent lime sludge to 50 per cent NH_4Cl being used.

For its manufacture, take the ammonium chloride crystals from the centrifuges and mix with them about an equal weight of caustic mud (from the caustic mud filters) washed free from caustic. The mixture, when still moist, is compressed to form noodles and chopped into short sticks to make granular ammonium chloride for the convenience of drilling on the farm. It is then dried in a small rotary furnace at a temperature below 300° C. The product is then sacked and sold to the farmers for fertilizer. Such a combination of $CaCO_3$ with NH_4Cl ensures a neutral mixture and does not render the soil acid. Often, however, farmers also mix some ammonium sulfate with it.

A. K. Ghose

Chapter XXVIII

Chemical Analyses and Tests in Alkali Industry

I. Soda Ash Manufacture

This chapter deals only with the analyses of the typical raw materials and finished products of the ammonia soda industry. The analyses of materials common to other industries, *e.g.*, coal, coke or water for boiler feed, will not receive consideration here, for they are discussed in standard books on Technical Analysis.

We shall give in each case (1) routine laboratory analyses, and (2) rapid tests for control work. The former are based on standard quantitative procedure, emphasis being laid on accuracy and reliability, while the latter, which only serve as a guide to aid operatives in the field, are generally more rapid, simpler, but less accurate methods. In the laboratory analyses, efforts have been made to determine as many substances as possible in one portion of the sample in order to save time. In places where two methods are equally well adapted, one possessing certain advantages over the other, both will be given and their merits or objections pointed out. In the control analyses, to save calculation it is recommended that reagent solutions of suitable strength be employed wherever possible so that, with a predetermined size of sample, the number of cc. of the reagent consumed represents directly the percentage of the constituent sought.

IA. Brine Laboratory Method

Brine is almost the universal form in which salt is secured for use in the ammonia soda industry. Where rock salt is the source of supply, it is always obtained in the form of brine, whether it comes from mines or wells as natural brine, as in Cheshire, England, or by pumping water down a bored hole to dissolve the salt below, as in Syracuse, N. Y., Barberton, O., Hutchinson, Kans., etc., in the United States. Where sea water is the source of supply, often solid crystals are first obtained by solar evaporation to eliminate many of the impurities in sea brine, and the crude salt so obtained is dissolved to make saturated brine. Sometimes concentrated sea brine is used.

In the routine laboratory analysis of salt the following determinations are made:

      (a) Specific gravity and temperature
      (b) Suspended matter
      (c) Ferric oxide and alumina

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(d) CaO
(e) MgO
(f) SO₃ } in one portion
(g) Na₂O and K₂O
(h) Total Cl⁻

(a) **Specific gravity and temperature.** Specific gravity is usually measured by a hydrometer (1.000-1.400 range) in a 500-cc. cylinder and the temperature is determined with a thermometer at the same time. Specific gravity readings must *always* be accompanied by temperature readings.

(b) **Suspended matter.** 500 cc. of the natural brine or 100 cc. of artificial sea brine before settling is filtered through a previously prepared and weighed Gooch crucible or porcelain filtering crucible and washed and dried at a temperature of 103 to 105° C. to a constant weight. The residue on the filter is the suspended matter.

(c) **Fe₂O₃ and Al₂O₃.** Pipette 25 cc. of the filtered sample into a 250-cc. volumetric flask and make up to the mark. Pipette 25 cc. into a 350-cc. beaker and dilute to about 100 cc. Heat to boiling. Add 2 grams NH₄Cl and make the solution slightly alkaline with NH₄OH. Filter off the precipitate by decantation, wash, ignite, and weigh. The residue is the combined oxides of Fe₂O₃ and Al₂O₃.

(d) **CaO.** Concentrate the filtrate to about 10 cc. Cool and add 15 cc. 6N (NH₄)₂CO₃ and 15 cc. 95 per cent alcohol. Stir vigorously and allow to settle in cold water for 30 minutes. Filter off the precipitate and wash with the (NH₄)₂CO₃ reagent. Evaporate the alcoholic filtrate on a water bath for SO₃ and Na₂O determinations (see below). Dissolve the precipitate with a little dilute hot HCl, pouring the acid repeatedly through the filter. Wash with hot water. Make the filtrate alkaline with NH₄OH, add 20 cc. $N/2$ (NH₄)₂C₂O₄ and boil. Set aside for 30 minutes. Filter, ignite strongly, and rapidly weigh the CaO.

Or, if preferred, the CaC₂O₄ precipitate after washing can be dissolved in dilute H₂SO₄ solution. The solution, after being heated almost to boiling, can then be titrated with $N/10$ KMnO₄.

(e) **MgO.** Concentrate the filtrate from the CaO determination to less than 75 cc., if the volume is larger. Cool and add 10 cc. N (NH₄)₂HPO₄ and one-third of the total volume of 6N NH₄OH. Stir vigorously and allow to settle in a cold place for four hours or, better, overnight. Filter, ignite in a porcelain crucible and weigh the Mg₂P₂O₇.

Or, if preferred, magnesium may be determined volumetrically by bringing the filtrate from the CaO determination to 70° C., adding 10 cc. 8-hydroxyquinoline solution, (25 g 8-hydroxyquinoline dissolved in 60 cc. glacial acetic acid and diluted to 2 l.) for each per cent MgO estimated to be present and then 4 cc. conc. ammonia solution (sp. gr. 0.90), and stirring continually with a mechanical stirrer for 15 minutes. Settle, filter and wash the pale yellow precipitate with hot 3 per cent ammonia solution. After washing, dissolve the precipitate in about 50 cc. hot 10

per cent HCl solution, and when solution is complete, dilute to 100 cc. and add 15 cc. conc. HCl (sp. gr. 1.20). Cool the solution to 25° C. and add from a burette 10 cc. $KBrO_3$-KBr solution (containing $\frac{1}{8}$ equivalent of $KBrO_3$ and KBr each) for each per cent of MgO estimated to be present. Stir the solution for 30 seconds to insure complete oxidation. Finally add 10 cc. 25 per cent KI solution, titrating the iodine with a standard sodium thiosulfate solution and using starch as indicator. The difference in the iodine values between the original $KBrO_3$-KBr solution and the back titration represents magnesium.

(f) **SO_3.** After alcohol is all evaporated from the $(NH_4)_2CO_3$ filtrate in (d), take up with water, acidify with HCl, adding 5 cc. dilute HCl in excess. Make the volume about 100 cc. and boil. Add 5 cc. N $BaCl_2$ in small drops with constant stirring. Digest on a steam bath for $\frac{1}{2}$ hour. Filter, ignite with moderate heat, and weigh the $BaSO_4$.

(g) **Na_2O and K_2O.** Make the filtrate alkaline with NH_4OH. Boil and precipitate Ba with a slight excess of $(NH_4)_2CO_3$. Filter by decantation and wash thoroughly. Evaporate the filtrate to dryness in a casserole and gently ignite off all ammonium chloride fumes over a small flame. Redissolve the residue with a little water and transfer to a tared platinum dish and ignite again. Weigh the residue as NaCl and KCl combined.

Dissolve the combined chlorides and make the volume of the solution 100 cc. in graduated flask. Take 10 cc. and dilute to 150 cc. in a 250-cc. beaker. Determine Cl in these combined chlorides according to Mohr's method described in (h) below. From the weight of combined chlorides and the quantity of total chlorine present, Na_2O and K_2O can be calculated.

(h) **Total Cl.** Pipette 10 cc. of the solution made in (c) for the Fe_2O_3 and Al_2O_3 determination and make up to 150 cc. in a volumetric flask. Pipette 10 cc. and dilute to about 100 cc. Titrate with $N/10$ $AgNO_3$ solution to a very faint red coloration, using 3 drops of 15 per cent K_2CrO_4 solution as indicator.

Other impurities, such as bromine, iodine, etc., that may be present in small quantities in sea salt are not determined.

For control work in the brine department the specific gravity reading by means of a hydrometer is generally sufficient. A saturated C. P. brine at room temperature has a specific gravity of 1.197. With impure brine such as sea brine the specific gravity may run as high as 1.205 to 1.215. Mohr's method is frequently employed in determining the concentration of brine used in operation. Operators often judge the degree of saturation of the brine by its Cl- content, as the sodium determination cannot be carried out by operatives in the field.

Note.—Mohr's method is sufficiently accurate with the size of the sample used if the volume of the solution to be titrated is diluted to about 100 cc. and if the very faintest red coloration is taken as the end point. The Volhard's method, however, using excess of $AgNO_3$ solution and titrating back with KCNS solution using ferric alum as indicator is generally considered more accurate.

An alternative method for the determination of Cl- using dichlorofluorescein is given toward the end of this chapter (see under "Alternative Laboratory Methods"). This method is accurate, especially when the quantity of the chlorides present is small.

IB. Solid Salt. Laboratory Method

The same methods are used in the analysis of solid salt except that moisture and combined water, or water of crystallization, are determined instead of specific gravity, and the insoluble matter instead of suspended matter.

(a) **Moisture and water of crystallization.** Weigh quickly to the nearest milligram a 5-gram portion of the crude salt sample. Dry to a constant weight, holding the temperature at 300° C. in a tared porcelain crucible until a constant weight is obtained. The loss of weight represents the moisture and all water of crystallization.

Note.— A temperature of 300° C is sufficient to decompose and drive out all water of crystallization from the crystals present. $MgCl_2$ $6H_2O$, however, if present will be decomposed to Mg_2OCl_2

(b) **Insoluble matter.** Weigh 10 grams of the crude salt and dissolve it in about 200 cc. of water. Filter in a tared Gooch crucible or porcelain filtering crucible, wash thoroughly and dry at 103 to 105° C. The residue is the insoluble matter.

For the other determinations, the same methods of procedure as given under brine analysis can be followed, but notice the size of the portions taken for analysis.

For calculations of the individual salts, the basic and acidic constituents are combined as follows: Combine all Na^+ with Cl^-; if Cl^- is in excess, combine it with Mg^{++}; if Mg^{++} is in excess, combine it with So_4^{--}; if SO_4^{--} is excess, combine it with Ca^{++}. If Na^{++} is in excess over Cl^-, combine the excess of Na^{++} with SO_4^{--}. Then if SO_3 is in excess, combine it with Mg^{++} and so on. Such combinations are purely hypothetical, guided by what is thought to be probably present when the various salts exist in solid form. Many combinations are possible with a given set of ionic constituents as determined by chemical analysis. This calculation, however, serves as a check on the accuracy of the work. If all constituents have been determined except those which, even if present, can only occur in very small quantities, the number of equivalents of the basic constituents should check with that of the acidic constituents, so that after all possible combinations have been made in the above calculation, no excess of either the acidic or the basic constituents should be unaccounted for. The discrepancy should not be greater than 0.10 per cent in any case, and the total should differ from 100 per cent by less than 0.15 per cent with the ordinary grade of salt.

II. Ammoniated Brine and Pre-carbonated Liquor

For laboratory analysis the following items are required:

(a) Specific gravity and temperature   (f) Cl

(b) Suspended matter   (g) SO_3

(c) CaO and MgO   (h) Total soluble sulfides

(d) Free NH_8 (i) CO_2

(e) Fixed NH_3

Ammoniated brine is the brine in which ammonia gas carrying some steam, CO_2, H_2S, etc., has been dissolved to the proper strength for the manufacture of $NaHCO_3$ and from which, consequently, calcium has been precipitated as $CaCO_3$ and magnesium as $MgCO_3$. This is responsible for the presence of fixed ammonia in the ammoniated brine. Excess of CO_2 is dissolved in it in the form of $(NH_4)_2CO_3$. H_2S is dissolved as such, or as $(NH_4)_2S$ or NH_4HS from combination with NH_3. Any ferric salts or iron scale are reduced to FeS and thrown out as greenish-black particles. Ammoniated brine usually has a faint yellowish or greenish-yellow tint due to a trace of FeS present in colloidal formation. Well-settled ammoniated brine should carry no suspended matter, no calcium salts, a very small magnesium precipitate, and only traces of FeS. Therefore these determinations, with the possible exception of Mg, are generally not necessary, unless specifically required.

(a) **Specific gravity and temperature.** Determine the specific gravity of the ammoniated brine with a hydrometer and take the temperature simultaneously.

(b) **Suspended matter.** If the suspended matter determination is required, filter 500 cc. of the ammoniated brine through a large, tared Gooch crucible or a porcelain filtering crucible, wash thoroughly, dry at 103 to 105° C. and weigh.

(c) **CaO and MgO.** If calcium and magnesium determinations are required, pipette 25 cc. of the ammoniated brine sample and make the volume about 100 cc. Bring to a boil and add 10 cc. $N/2$ $(NH_4)_2C_2O_4$ with constant stirring. Set aside for 30 minutes. Filter, ignite strongly and weigh the CaO quickly.

For MgO determination, follow exactly procedure (c) under Brine Analysis.

(d) **Free NH_3.** Pipette 25 cc. of the original sample and make up to 500 cc. in a volumetric flask for analyses (d) to (i). Pipette 25 cc. of this solution into a 250-cc. distilling flask provided with a condenser, and add 50 cc. distilled water without adding any NaOH. Distill into a 250-cc. Erlenmeyer flask containing 100 cc. $N/10$ HCl until the volume in the distilling flask is about 30 cc. Titrate the excess of HCl in the Erlenmeyer flask with $N/10$ NaOH.

(e) **Fixed NH_3.** Introduce 25 cc. $N/2$ NaOH into the contents of the distilling flask after the free ammonia determination and distill similarly into another Erlenmeyer flask containing 50 $N/10$ HCl. Titrate the excess of HCl similarly.

(f) **Cl.** Pipette 10 cc. of the above dilute solution. Neutralize the alkalinity with HNO_3, using one drop of 0.1 per cent methyl orange as indicator. Introduce about 0.2 gram of C. P. $CaCO_3$ powder and stir vigorously. Dilute to about 100 cc. and titrate the $CaCO_3$ suspension with $N/10$ $AgNO_3$ until a faint red coloration is just visible, using 3 drops of 15 per cent K_2CrO_4 as indicator.*

---

* With the introduction of a small amount of $CaCO_3$, the excess acid is neutralized and the solution brought to the exactly neutral condition. Under such conditions, the end point of Ag_2CrO_4 is sharper. In place of Ag_2CrO_4 sodium arsenite solution can be used as indicator.

(g) **SO₃.** Pipette 10 cc. of the above solution. Acidify with dilute HCl, using 5 cc. in excess. Bring to a boil and add 5 cc. N BaCl₂ with constant stirring. Filter the BaSO₄, ignite with moderate heat and weigh.

(h) **Total soluble sulfides.** Pipette 25 cc. of the solution. Neutralize with dilute HCl in the cold and immediately titrate with $N/10$ I₂ solution, using starch as indicator.**

(i) **CO₂.** Pipette 15 cc. of the solution, and determine CO₂ gas in the apparatus illustrated (Fig. 123), taking the temperature of the jacket water. Read the barometric pressure. One cc. CO₂ gas under standard conditions weighs 0.0019763 gram.
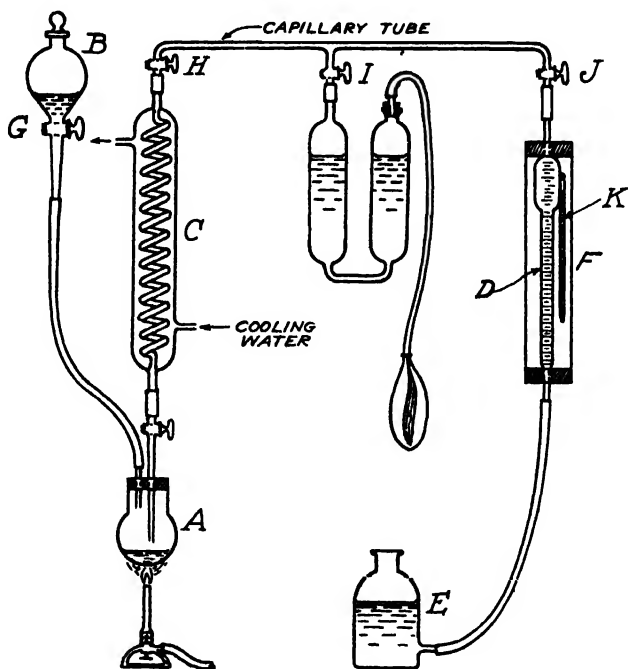
Fig. 123. Apparatus for carbon dioxide determination by expulsion and absorption.

Procedure: Place 15 cc. of the above solution in a 100-cc. generating flask A. Run into this flask 15 cc. of $6N$ H₂SO₄ from funnel B. Heat to boiling, and collect CO₂ gas through the spiral condenser C into the burette D provided with water jacket F; meanwhile cock I remains closed. When all the gas has been driven out, fill the flask A and the condenser C with water through funnel B so that water rises to cock H. Now close the cock H. With the levelling flask E, read the volume of CO₂ in the burette D. Record the thermometer reading T (thermom-

** High results would be obtained if the ammoniated brine solution is directly titrated with I₂ solution without first neutralizing it with an acid.

eter K), and the barometric reading P_1. Open the cock I and bring the gas into the absorption flask containing NaOH solution. Take the volume of the remaining gas in burette D again. Loss in volume V_1 represents CO_2. Let a = aqueous tension at T °C. in mm. Hg.

$$V \text{ (under standard conditions)} = V_1 \times \frac{P_1 - a}{760} \times \frac{273}{273 + T}$$

For control work for the carbonated and green liquors in the tower house, the ammoniated liquor in the absorber house, or the filter liquor in the distiller house, the following determinations are required:

(1) Free NH_3
(2) Total Cl
(3) H_2S
(4) CO_2

FIG. 124.

Apparatus for carbon dioxide tests in control work.

A is 200 cc. burette, graduated in ¼ cc.

B is plain levelling tube of large bore (20 mm.)

C is rubber tubing, 5 mm. bore.

D is generating flask, containing "E."

E is a short glass tube of 10 cc. capacity, closed at the bottom, E being embedded in paraffin "F."

F is paraffin to hold E in position by pouring molten paraffin and allowing it to solidify.

G is long rubber tubing, 5 mm bore.

H is rubber stopper with 1 hole.
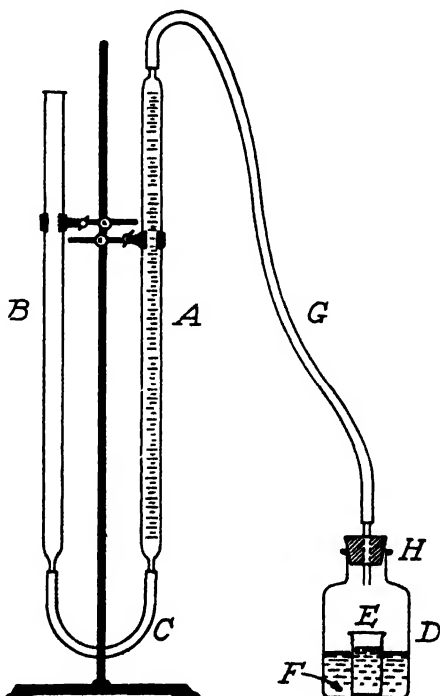
The tests may be made in the field by men having no special chemical training. All they require is rough information to guide their operations in the field, and that information must be at hand quickly when desired. Simplicity and rapidity are of paramount importance. Frequently the figures do not represent exact results, but they give comparative values which are sufficient to enable the operators to fix and duplicate the operating conditions. All the results are calculated to "titer" or the number of cc. of any normal solution per 20 cc. sample.

Pipette 10 cc. of the strong liquor, mother liquor, or any other liquor, in a 100-cc. graduated flask and make up to the mark.

(1) *Free NH₃.* Pipette 10 cc. of the diluted solution and titrate against N H_2SO_4 using methyl orange as the indicator. The result multiplied 20 times gives the "free NH_3 titer."

(2) *Total Cl.* After the free NH_3 determination, drop in 0.2 gram C. P. $CaCO_3$ powder, dilute the same portion to about 100 cc. Add 3 drops of 15 per cent K_2CrO_4 solution and titrate against a N $AgNO_3$ solution until a faint red coloration is seen. The result multiplied by 20 gives the "chlorine titer."

(3) *H_2S.* Pipette 20 cc. of the original sample, neutralize with H_2SO_4 until neutral to methyl orange indicator. Titrate immediately against $N/10$ I_2 solution, using starch as indicator. The result divided by 10 gives the "sulfide titer."

(4) *CO_2.* Determine the volume of CO_2 dissolved in the liquor as follows (Fig. 124).

Procedure: Pipette 10 cc. of the diluted solution into E and carefully introduce 10 cc. $6N$ H_2SO_4 into the space outside E on the paraffin bottom. Place the stopper tightly. Level A and B. Record reading on A. Invert flask D and shake thoroughly. Immerse flask D in a vessel of water at room temperature for a few minutes. Level A and B again and take reading on A. The increase in volume represents CO_2. The result multiplied by 20 gives the volume titer of CO_2 at room temperature.

IIIA. Limestone. Laboratory Method

(a) Moisture	⌐(g) K_2O
(b) Silicious matter	⎰(h) Na_2O
(c) Total silica	⌊(i) CO_2
(d) Fe_2O_3, Al_2O_3, (TiO_2 and P_2O_5)	(j) Cl
(e) CaO	(k) SO_3
(f) MgO	

Preparation of Sample:

Samples of limestone are taken from each carload in about the same size, taking in different varieties. The stones are then crushed in a small jaw crusher to about 1 inch in size and quartered successively until about a 10-lb. lot is obtained. Instead of quartering, a mechanical sampler, if available, affords a more rapid and better means of sampling. The sample is crushed to 4 mesh in roller crushers and then pulverized to −20 mesh in a disc pulverizer. Of this a 0.5-lb. portion is taken and sent to the laboratory.

If the above equipment is lacking, the samples of limestone from the carloads are broken by hand, quartered as before, and the final portion crushed in a small jaw crusher operated by hand. This crushed sample is now pulverized in a porcelain mortar to 20 mesh.

(a) **Moisture.** Heat a 0.5-gram sample prepared as above in a tared porcelain crucible at 105° C. for 1.5 hours or to a constant weight. The loss in weight represents moisture.

(b) **Silicious matter.** Transfer the dried sample from (a) to a 250-cc. wide-mouthed flask. Add 30 cc. water and 25 cc. N HCl in small portions, covering the mouth of the flask with a small watch glass. When effervescence has subsided, transfer to a 200-cc. casserole and evaporate just to dryness. Dehydrate at 125° C. for 1 hour. Take up with 10 cc. $6N$ HCl, heat to dryness and dehydrate once more. Take up with 10 cc. $6N$ HCl and 50 cc. water, heat to boiling and filter. Wash the residue with hot water until free from chlorides, collecting the washing with the main filtrate for the determination of combined oxides [see (d) below].

(c) **Total silica.** Fuse the silicious matter with 4 times its weight of Na_2CO_3 and 4 times its weight of K_2CO_3 in a platinum crucible. While it is still molten, tilt the crucible to spread the melt up the sides, so that when cold the mass can be readily loosened. Transfer the mass to a 250-cc. casserole, washing the contents of the crucible into the casserole. Acidify very carefully with $6N$ HCl. When effervescence subsides add 5 cc. more. Evaporate to dryness and determine the silica by double dehydration as in (b) above.

(d) **Fe_2O_3 and Al_2O_3 ($TiO_2 + P_2O_5$).** Combine the filtrates from (b) and (c). Add 2 grams NH_4Cl and make the solution very slightly alkaline with $6N$ NH_4OH. Heat to boiling. Filter by decantation, wash the precipitate and ignite. The residue is the combined oxides of iron and aluminum with P_2O_5 and TiO_2 if phosphorus and titanium are also present.

(e) **CaO.** Heat the filtrate from the above and add 20 cc. $N/2$ $(NH_4)_2C_2O_4$ with stirring. Set the beaker over a hot plate for 30 minutes. Filter, test the filtrate with a small amount of $(NH_4)_2C_2O_4$ and ignite first gently and finally strongly over a Meker burner. Cool in a desiccator and weigh the CaO quickly.

Note.—An alternative method for the determination of calcium after the precipitation of CaC_2O_4 is to dissolve the washed oxalate on the filter with hot, dilute H_2SO_4, wash with hot water, warm up the solution to about 80° C. and titrate with 0.10N standard ceric ammonium sulfate solution, using one drop of orthophenanthroline-ferrous sulfate solution as the indicator, until one drop of the ceric ammonium sulfate solution discharges the pale pink color.

(f) **MgO.** Evaporate the filtrate to not more than 75 cc. While hot, precipitate $Mg(NH_4)PO_4$ with 10 cc. N $(Na_2)HPO_4$ and $\frac{1}{3}$ of the volume of 1.12 NH_4OH. Stir vigorously and allow to settle in ice water for 4 hours or preferably in cold water overnight. Filter by decantation, wash and ignite the precipitate in a tared porcelain crucible. The residue is $Mg_2P_2O_7$.*

(g, h) **K_2O and Na_2O.** Weigh another 0.5 gram portion and mix it thoroughly with an equal amount of NH_4Cl on a glazed paper. Then mix with 8 times its weight C. P. $CaCO_3$ powder, reserving a small portion of $CaCO_3$ for "washing." Place the intimate mixture in a platinum crucible and cover the crucible. Heat very gently for 15 minutes so that

* For careful work re-dissolving of $MgNH_4PO_4$ with an acid and reprecipitation from the solution is necessary.

no NH_4Cl fumes appear but the ammonia odor is noticeable. Then heat with a very short flame for 45 minutes so that only the lower third portion of the crucible becomes red. Then cool and disintegrate the mass in 200 cc. of water in a 500-cc. casserole. Heat to boiling and filter by decantation. Repeat the extraction and wash the residue until free from chlorides. Acidify with $6N$ HCl and add 5 cc. in excess. Bring to boiling, add N $BaCl_2$ solution drop by drop until no further precipitate is formed, avoiding a large excess. Make the solution alkaline with ammonia and add a slight excess of $6N$ $(NH_4)_2CO_3$. Concentrate the solution to about 100 cc., filter and wash with hot water. Add $N/2$ $(NH_4)C_2O_4$ drop by drop and see if any precipitate occurs. If so, add a small excess, boil and filter. Evaporate the filtrate to dryness and ignite off NH_4Cl in a casserole with a moderate heat. Take up with 10 cc. $6N$ HCl and re-ignite. Dissolve with a little water, transfer and wash into a tared porcelain dish. Evaporate to dryness over a steam bath, protecting the dish from foreign matter. Finally dry in an oven at 105° C. The residue is the combined chlorides of sodium and potassium.

If sodium and potassium are to be determined separately, dissolve the combined chlorides making the volume 150 cc. Determine the chloride by Mohr's method and calculate Na_2O and K_2O from the two results.

(i) **CO_2.** CO_2 may be determined in four ways, (1) by decomposition with an acid and titration, (2) by evolution and measuring the volume of the gas as in (i) under Ammoniated Brine analysis, (3) by expulsion of CO_2 from a weighed flask and determining the weight of the CO_2 lost by difference, and (4) by evolution and weighing the absorbed gas. Of these the first is the least accurate even when a non-volatile acid such as H_2SO_4 is used for decomposition, because in titrating back with an alkali, when the end point is registered even by methyl orange, a certain amount of acid from hydrolyzable salts, *e.g.*, Mg^{++}, Fe^{+++}, Al^{+++}, Ti^{++++}, etc., salts, which form insoluble hydroxides with an alkali, will have inevitably been included. But its rapidity has much to commend it for quick, rough tests.

The second method by the measurement of the volume of CO_2 together with absorption in an Orsat pipette is often used for determining CO_2 in solution such as in ammoniacal liquors (see (i) under Ammoniated Brine analysis). The result calculated from the volume of CO_2 obtained is less than 5 in 1000 or 0.5 per cent, too low. In the case of limestone, however, the very large volume of CO_2 liberated makes it difficult to handle, and for this reason the method is seldom used.

The third method by the expulsion of CO_2 and weighing the loss in weight in various forms of alkalimeters such as Mohr's, may be used for limestone or alkali carbonates. This method gives fairly accurate results (accurate to 0.1 per cent), provided that the gas, after liberation, is driven out not by heating but by air bubbling in the cold.* The arrangement is shown in Fig. 125.

* See "Determination of Carbon Dioxide in Carbonates" by W. W. Scott and P. W. Jewel, *Ind. Eng. Chem., Analytical Ed.*, Jan. 15, 1930.

Procedure: Weigh the thimble *B* and into it weigh about a 0.5-gram sample. Disconnect the Erlenmeyer flask at *G* together with the rubber tubing and pinch cock, close the cock *G* and weigh the Erlenmeyer flask with the acid, $CaCl_2$, and tube *F*, etc., complete. Place the thimble with the sample into the solution in the flask. Tip the flask so as to overturn the thimble to allow the acid to react with the sample. Set aside for a few minutes. When the reaction has subsided, connect *C*, *D* and *E*. Open the cock *G*. Apply suction for about 15 minutes. Disconnect at *G*. Weigh the complete set of apparatus again. The loss in weight represents CO_2.
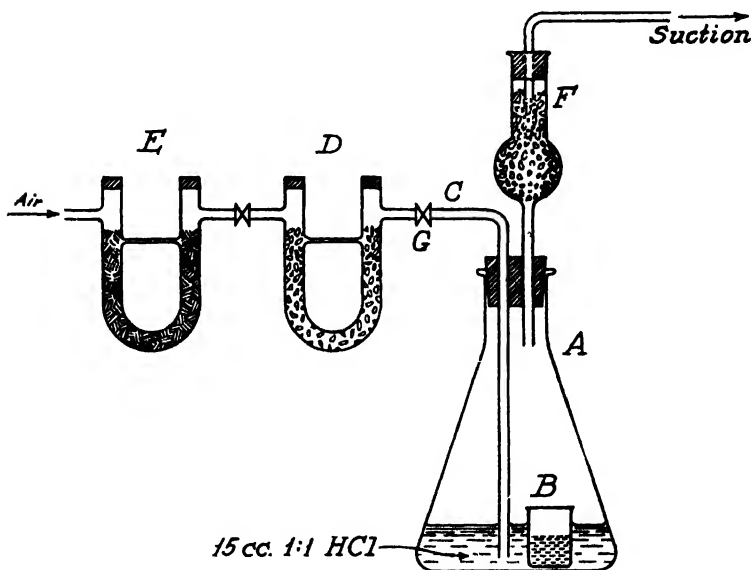
Fig. 125. Apparatus for determining carbon dioxide by expulsion and weighing.

A = 50 cc. Erlenmeyer flask containing 15 cc. 1:1 HCl.
B = Small glass thimble for a ½ gram sample.
C = Small gas tubing bent at right angles and passing through a 2-hole rubber stopper with the end dipped into HCl solution drawn to a capillary tip.
D = U-tube containing $CaCl_2$ (granular, about 8 mesh).
E = U-tube containing soda lime.
F = A straight $CaCl_2$ guard tube.
G = Short rubber tubing with a small pinch cock.

This method has drawbacks in that any other volatile gas set free by the acid will be included in the CO_2 determination.

The fourth method by weighing the CO_2 absorbed is the most accurate (Fig. 126). It measures CO_2 alone in the liberated gas, but unfortunately the method is long and tedious. It is used only when accurate results are desired.

Arrangement of apparatus by the fourth method is as follows:
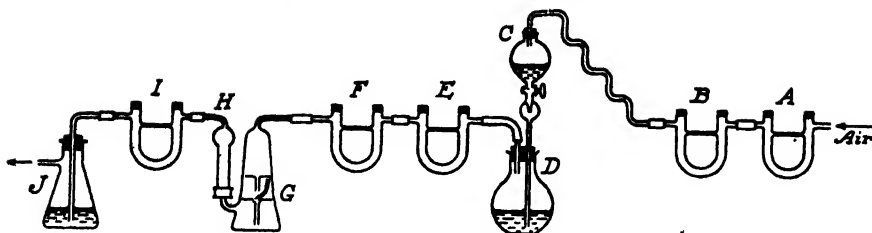
Fig. 126. Absorption train for carbon dioxide determination.

A, B = U-tubes containing soda-lime to absorb CO_2 from air.
C = Dropping funnel for dropping in 20 cc. $2N$ HCl.
D = Generating flask (150 cc. Soxhlet extraction flask).
E = U-tube containing anhydrous $CaCl_2$ to absorb aqueous vapor carried over from the generating flask.
F = U-tube containing anhydrous $CuSO_4$ to absorb HCl, H_2S, carried over from the generating flask.
G = Gomberg bulb containing (1:2) KOH in each compartment.
H = Guard tube containing ⅓ of its length soda-lime, ⅓ solid KOH and ⅓ anhydrous $CaCl_2$ for retaining moisture and CO_2 from Gomberg bulb.
I = U-tube containing anhydrous $CaCl_2$ to absorb any moisture that may be forced back from suction flask.
J = Suction flask.

Procedure: Weigh a 0.5-gram sample into the generating flask and cover it with 30 cc. water. Connect the apparatus as in the diagram except that G, H are disconnected for weighing and that the $2N$ HCl is not put in the dropping funnel. While G, H are being weighed, apply suction to this system to exhaust any CO_2 from the air in the system. After weighing insert G and H in the train, fill the dropping funnel with 20 cc. $2N$ HCl. Without opening the drop cock in the dropping funnel apply suction to test if the system is air-tight. Then drop in $2N$ HCl slowly so that the gas bubbles through the Gomberg bulb at a rate not faster than 2 bubbles per second. When all the acid has been dropped in and no more CO_2 is apparently liberated from the generating flask, heat the generating flask very gently just to boiling and continue to draw air through the system to exhaust all CO_2. Disconnect G and H, wipe clean and weigh. Remove the flame. The increase in weight represents CO_2. One cc. CO_2 under standard conditions weighs 1.9763 mg.

(j) **Cl.** Weigh another 0.5-gram sample in a wide-mouth, 250-cc. Erlenmeyer flask, add 20 cc. water and 20 cc. $2N$ H_2SO_4 slowly. When effervescence ceases, heat to boiling for 5 minutes. While hot, make the solution slightly alkaline with $6N$ NH_4OH with constant stirring. Filter first by decantation into a 250-cc. volumetric flask, and wash the precipitate in the Erlenmeyer flask several times with hot water. Cool the filtrate and make the volume to the 250 cc. mark. Pipette 100 cc. into a 250-cc. beaker, and neutralize the solution carefully with a small amount of H_2SO_4. Add about 0.2 gram pure $CaCO_3$. Determine chlorine by Mohr's method in the usual way.

(k) **SO_3.** Weigh another 0.5-gram sample and fuse it with 4 times its weight of Na_2CO_3 and K_2CO_3 each. Dissolve the melt by boiling in

about 100 cc. water in a 250-cc. casserole with an excess of $6N$ HCl added in small portions, avoiding loss by effervescence. Evaporate the solution to dryness and bake at 130° C. for 1 hour; moisten with 5 cc. concentrated HCl and bake again for 0.5 hour. Add 100 cc. of water and bring to boiling. Filter and wash the residue. Neutralize the filtrate with $6N$ HCl, add 5 cc. in excess and heat to boiling. Add 5 cc. N $BaCl_2$ in drops, stirring constantly. Allow to settle on a hot plate for about $\frac{1}{2}$ hour, filter and ignite slowly so as not to allow the filter paper to burn in flames. Cool and add a drop or two of $6N$ H_2SO_4. Ignite for weighing.

In order to avoid unreliability in sampling, the milk of lime made from the limestone burned is analyzed completely by the methods described. The amount of $CaCO_3$ and $MgCO_3$ calculated from these results better represents the average, although the lime contains a small amount of ash (1-1.5 per cent) from the coke introduced in the kiln.

IIIB. Rapid Analysis

When rapid analyses are required as in the case of exploring limestone deposits when 50 or more field samples are to be tested and only comparative results are desired, the following procedure is followed:[*]

Weigh a 0.5-gram dried pulverized sample in a wide-mouth 250-cc. Erlenmeyer flask, wash down with a little water and introduce 25 cc. $N/2$ HCl. Stopper the flask with a one-hole rubber stopper carrying a glass tubing about 24 inches long. Heat very gently to boiling. Cool in water and wash down the flask with a little water. When the solution has cooled, add a drop of methyl orange and titrate the excess acid with $N/5$ NaOH, taking the first change from a pink to a yellowish color or colorless as the end point. The loss in acidity represents CO_2.

To the solution add 10 cc. $2N$ NH_4Cl and a small amount of ammonia to give a distinct odor. Heat to coagulate the precipitate. Filter through a tared porcelain filtering crucible, and wash the residue and precipitate. Dry at 105° C. to a constant weight and weigh. The difference represents silicious matter and iron, aluminum, titanium, phosphate, etc. The assumption is made that the sum of $CaCO_3$, $MgCO_3$, the insoluble matter, and ammonia precipitate equals 100 per cent in the dried sample.

Let $C = \%$ $CaCO_3$

$M = \%$ $MgCO_3$

$R = \%$ Residue and ammonia precipitate

$$\text{Total } CO_2 \text{ as } CaCO_3 = \text{cc. } N/2 \times \frac{0.025}{0.5} \times 100$$

$$= \text{cc. } N/2 \text{ HCl} \times 5 = A$$

$$\text{Then } C = A - \frac{100\,M}{84.32}$$

$$M + C + R = 100\%$$

$$\therefore M = 5.38\,(A + R - 100)$$

$$\text{and } C = A - 1.19\,M$$

[*] Based on a paper by S. D. Averitt, *J. Eng. Ind. Chem.*, **14**, 1139 (1922).

The suitability of a new supply of limestone for ammonia soda manufacture is determined by the content of $CaCO_3$, $MgCO_3$ and silicious matter in it. Excessive quantities of silicious matter tend to form fusible clinkers blocking the lime kiln or attacking the kiln lining. The rapid analysis, while not strictly accurate, is sufficient to determine the suitability of limestone for the ammonia soda industry.

The physical appearance of limestone as regards color, luster, striations, structure, etc., varies a great deal, depending upon the locality. Probably the age, manner of formation, etc., have much to do with its physical characteristics.

In the lime department the operators may judge the strength of the milk of lime by means of a specific gravity bottle, which is a tared bottle with 100 cc. marked on it. The net weight in grams divided by 100 represents the specific gravity. With the strength of milk of lime as high as 250 grams CaO per liter, the suspension is so thick that the use of a hydrometer is not feasible. The specific gravity determination is a very rough guide because the specific gravity does not represent accurately the strength of milk of lime unless the limestone burned is of uniform quality, and of uniform grade, which is seldom true even within the same quarry. In all cases the operators are required to determine the actual lime content in order to check the specific gravity reading. For this purpose, a 5-cc. portion of milk of lime from a well-shaken sample is taken with a pipette having the capillary tip cut off and a new mark made by recalibration. Titrate the milk of lime with N H_2SO_4 using phenolphthalein as indicator. The first appearance of red coloration in the solution is taken as the end point in the practical work.

Milk of lime is tested by the operators in the lime department, in the distiller house, and in the causticizing room when milk of lime is used for causticization.

IV. Kiln Gas and Returned Gas from Dryers

The CO_2 gas is analyzed for
  (1) CO_2
  (2) O_2
  (3) CO
  (4) N_2 (by diff.), in the order named

For this purpose, a 3-pipette Orsat apparatus is sufficient. Sodium hydroxide solution is used for the CO_2 determination, an alkaline solution of sodium pyrogallate for the O_2 determination, and acid or ammoniacal cuprous chloride solution for the CO determination. The methods of preparing these reagents are as follows:

(1) Sodium hydroxide: Dissolve 350 grams of NaOH stick in a liter of water.

(2) Alkaline sodium pyrogallate: Dissolve 350 grams of NaOH stick in a liter of water and then 50 grams of solid pyrogallic acid.

(3) Cuprous chloride:

(a) Acid solution.*—Place a layer of copper oxide about ⅜ inch thick in a 2-liter bottle and a bundle of 20 $\frac{1}{32}$-inch (or No. 20) copper wires about 8 inches long each. Fill the bottle with 1.10 HCl so as to leave no air space when the stopper is put in place. Invert the bottle and set aside with frequent shaking until the solution is almost colorless.

(b) Ammoniacal solution.—The acid cuprous chloride is made slightly alkaline with 0.90 ammonia and a bundle of copper wires is put in. The bottle is set aside as before.

The manipulation of the Orsat apparatus is simple and will not be described here. Where hourly analyses are made, the above solutions must be changed not less than once a week. The cuprous chloride and pyrogallate solutions must be tested more frequently to determine whether they are still good.

At present, cuprous-ammonio formate solution, especially in the cold, is considered to be a very good absorbing agent for carbon monoxide.

When CO_2 gas to be analyzed carries NH_3, such as in the furnace gas or tower exit gas, the gas must be washed through a washing bottle containing H_2SO_4 before entering the Orsat apparatus.

V. Crude Ammonia Liquor

This is probably the cheapest source of ammonia for the ammonia soda industry. Ammonia in the liquor is mostly in the form of $(NH_4)_2CO_3$ or NH_4HCO_3, and some in the form of $(NH_4)_2S$ or NH_4HS. The percentage of sulfide present should be kept as high as possible. Concentration of ammonia in the liquor is from 16 to 25 per cent NH_3 by weight. For the ammonia soda industry we are interested in the total ammonia content and the sulfide (or total reducing sulfur). Calculate the sulfide arbitrarily to 60 per cent Na_2S and ammonia to 25 per cent ammonium sulfate (25 per cent NH_3).

(a) **Total ammonia.** Pipette 25 cc. of the crude liquor into a 500-cc. volumetric flask and make it up to the mark. Place 10 cc. in a 150-cc. distilling flask and distill with the addition of a small amount of NaOH solution, absorbing the gas in 100 cc. $0.10N$ H_2SO_4 in a 250-cc. Erlenmeyer flask. Titrate the excess of acid with $0.10N$ NaOH, using methyl orange as the indicator.

(b) **Total reducing sulfur.** Pipette 25 cc. of the above diluted solution in a 250-cc. Erlenmeyer flask, acidify with $6N$ HCl and immediately titrate with $N/10$ I_2, using starch solution as the indicator. This represents sulfide, thiosulfate, etc.

(c) **Sulfide sulfur.** Pipette 25 cc. of the diluted solution into a 150-cc. Erlenmeyer flask and dilute to about 50 cc. Titrate with $0.10N$ $ZnSO_4$

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* The absorption power of the acid solution is lower than that of the ammoniacal solution. See "Absorption of Carbon Monoxide by Cuprous Ammonium Salts" by W. Gump and I. Ernst, *Ind. Eng. Chem.*, Vol. 22, Apr. 1930, p. 382.

testing the formation of the white precipitate by a drop of $ZnSO_4$ solution. Titrate until a drop from the clear solution on the stirring rod gives no immediate brown spot on a piece of lead acetate paper (filter paper impregnated with 10 per cent $PbAc_2$ solution).

(d) **CO_2.** See (i) under Limestone analysis, or (i) under Ammoniated Brine analysis.

For control work, only the total ammonia and total reducing sulfur determinations are made.

VI. Sodium Sulfide

The function of a soluble sulfide in the ammoniated brine is to give a coating of FeS in all iron apparatus, which protects the surface of the iron from being attacked by the ammoniated brine, because FeS is quite inert in alkaline solutions. Sometimes the amount of sulfide in the crude liquor introduced daily into the system is not sufficient. Some sulfide (usually a solution made of 60 per cent fused Na_2S) must then be added to the distiller feed liquor in order to maintain a good color in the soda ash. Too much sulfide (from the use of too much Na_2S), on the other hand, is decidedly harmful because excessive sulfide in the ammoniated brine is corrosive and tends to dissolve iron from the apparatus. Ammoniated brine having a high sulfide content will have a dark green coloration or residue from contact with the iron surface in the apparatus, for instance, in the settling vats.

In the laboratory the per cent Na_2S is tested. For this purpose some fragments of fused Na_2S of about 5 grams weight are weighed and dissolved to make 500 cc. of solution in a volumetric flask. A 15-cc. sample of this solution is placed in a 250-cc. flask, 10 cc. N NH_4OH and 5 cc. N NH_4Cl are added, and the solution is diluted to about 50 cc. Proceed as in (c) under Crude Ammonia Liquor analysis above.

For control work in the field, the operators test the strength of the Na_2S solution by titrating a sample for total reducing sulfur as in (b) under Crude Ammonia Liquor analysis. This, of course, includes sodium thiosulfate, sodium sulfite, etc., besides sodium sulfide, if the former are present in the fused sulfide.

VII. Tower Draw Liquor (Mother Liquor)

This is the clear portion of the liquor from which sodium bicarbonate has completely separated out at the temperature of the draw. It is from the analysis of this liquor that we can determine the percentage conversion of $NaCl$ into $NaHCO_3$ in the towers ("percentage decomposition"). Unfortunately, the nature of the substances present in the mother liquor is exceedingly complex and there are at least nine different combinations present in solution in equilibrium with one another. The study of these compounds or combinations in their exact relationship has formed the subject matter of a special chapter, and the exact methods of laboratory analysis will not be discussed here (see Chapter XI). The following

represents the partial and approximate analysis commonly required in ammonia soda works.

(a) Specific gravity and temperature   (f) SO_3

(b) Free NH_3 (or total alkalinity)   (g) Total Cl

(c) Fixed NH_3 (h) Unconverted salt (NaCl)

(d) CO_2 (i) Percentage decomposition

(e) Soluble sulfide

(a) **Specific gravity and temperature.** These are determined with a 1.000-1.400 hydrometer and a thermometer simultaneously.

(b) **Free NH_3.** This, as usually carried out in the laboratory or in the field, comprises not only NH_4OH, but also $(NH_4)_2CO_3$, NH_4HCO_3, $NaHCO_3$, etc.

For analysis, pipette 25 cc. of the liquor and make it up to 500 cc. in a volumetric flask. Twenty-five cc. of this diluted sample are taken and the procedure given in (d) under Ammoniated Brine analysis can be followed.

Note.—At first thought, it might appear that the determination of free ammonia in the mother liquor by distillation without the addition of caustic soda would give the true value of free ammonia present and would be more accurate than by plain titration for alkalinity with an acid using methyl orange as indicator. But it will be shown below that both methods amount to the same thing and determine the total alkalies in the mother liquor. For, in titration with an acid using methyl orange, we are titrating not only NH_4OH but $(NH_4)_2CO_3$, NH_4HCO_3, $NaHCO_3$, etc.; but in distillation the same substances either yield free ammonia or react with NH_4Cl to give free ammonia by heating. Thus,

$$(NH_4)_2CO_3 \rightarrow 2NH_3 + CO_2 + H_2O$$
$$NH_4HCO_3 \rightarrow NH_3 + CO_2 + H_2O$$
$$NaHCO_3 + NH_4Cl \rightarrow NH_3 + CO_2 + NaCl + H_2O$$
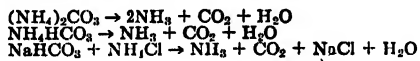
The two methods are really identical and the titration method is the shorter of the two.

(c) **Fixed NH_3.** Procedure (e) under Ammoniated Brine analysis is followed.

(d) **CO_2.** Procedure (i) under Ammoniated Brine analysis is followed.

(e) **Sulfide.** Procedure (h) under Ammoniated Brine analysis is followed.

(f) **SO_3.** Procedure (g) under Ammoniated Brine analysis is followed.

(g) **Total Cl.** Procedure (f) under Ammoniated Brine analysis is followed.

(h) **Unconverted salt (NaCl).** This, as is usually carried out in the laboratory, comprises not only NaCl as such but also an equivalent quantity of $NaHCO_3$ from its reaction with NH_4Cl present in the mother liquor.

$$NH_4Cl + NaHCO_3 \rightarrow NaCl + NH_3 + CO_2 + H_2O$$
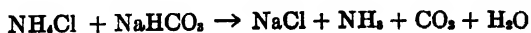
For analysis, pipette 25 cc. of the diluted sample and evaporate it in a tared platinum dish. Gently ignite the residue until no more ammonium chloride fumes are seen. Cool and weigh. This, less the equivalent quantity of Na_2SO_4 from (f) above, may be taken as NaCl, assuming

magnesium salts as entirely absent and all $(NH_4)_2SO_4$ completely converted to Na_2SO_4 by ignition in the presence of $NaHCO_3$.

Note.—When the total Cl and the fixed NH_3 in the mother liquor are known, an approximate value of the unconverted NaCl may be calculated as follows: Calculate fixed NH_3 to NH_4Cl, deduct from the total Cl the amount of Cl in NH_4Cl and calculate the rest of Cl to NaCl which can be taken roughly as the unconverted salt.

(i) **Percentage decomposition.** This represents the percentage of NaCl that has been converted to sodium bicarbonate in the towers and is roughly calculated as follows:

$$\% \text{ decomposition} = \frac{\text{Na in } NaHCO_3 \text{ formed}}{\text{Na in } NaHCO_3 \text{ formed} + \text{Na in unconverted salt}} \times 100$$

$$\text{or} = \frac{\text{Total Cl} - \text{Cl in unconverted salt}}{\text{Total Cl}} \times 100$$

$$\text{or} = \frac{\text{Fixed } NH_3 \text{ formed in towers}}{\text{Total Cl}} \times 100$$

All quantities must of course be expressed in the number of equivalent weights per liter or in titers. It is at best an approximation but represents the method usually carried out in the laboratory of an ammonia soda works.

For the filter liquor, the analysis follows the same scheme as for the tower draw liquor. A comparison of concentrations of total chlorine in the filter liquor and in the draw liquor will show the extent of dilution by the filter wash water; hence the amount of water used on the filters. This filter liquor can be sampled and analyzed at different points on its way to the distillers to follow up the extent of dilution by the various condensates or liquors introduced at these points.

If the approximate percentage of decomposition only is to be determined, the following rough but very rapid procedure can be employed.

VIIA. Tower Draw Liquor (Alternative Method)

Pipette 10 cc. of the clear mother liquor into a 150-cc. evaporating dish, evaporate just to dryness over a steam bath, and dry to a constant weight in an electric oven at 105° C. Weigh the contents of the dish. Ignite the contents over a low gentle flame until all ammonium chloride fumes disappear. Cool and weigh again. The contents of the first weighing can be taken as $NaCl + NH_4Cl$ and that of the second weighing as NaCl, so that the difference is NH_4Cl and

$$\% \text{ decomposition} = \frac{NH_4Cl}{NaCl + NH_4Cl} \times 100$$

VIII. Crude Bicarbonate from Filters and Refined Bicarbonate of Soda

The crude sodium bicarbonate from the carbonating towers, while a very pure product from the commercial standpoint, contains a small amount of NH_4HCO_3, $NaCl$, NH_4Cl and sometimes also $MgCO_3$. Magnesium carbonate will be present if the brine contains an excessive amount of magnesium salts, as sea brine does, inasmuch as it is very difficult

to get rid of the last trace of magnesium precipitate in the ammoniated brine. Calcium, however, is very seldom present, because $CaCO_3$ settles out quite readily in the settling vats. The small amount of NH_4Cl from the mother liquor contained in the bicarbonate behaves in the ordinary analysis as if it were NH_4HCO_3, for free ammonia will be given off from its reaction with $NaHCO_3$ during drying or distillation, or whenever the solution is heated.

$$NaHCO_3 + NH_4Cl \rightarrow NaCl + NH_4HCO_3 \rightarrow NaCl + NH_3 + CO_2 + H_2O$$

Therefore, in order to determine NH_4Cl, absolute alcohol is used to extract NH_4Cl from the crude bicarbonate, the carbonates and bicarbonates of sodium and ammonium being very sparingly soluble in absolute alcohol. From the alcoholic extraction excess alcohol and free ammonia (if any) are driven off by evaporation over a steam bath, leaving behind NH_4Cl. By far the greatest part of the "free ammonia" in the mother liquor, or in the bicarbonate separating out from the mother liquor, exists as NH_4HCO_3. The evidence is that the mother liquor gives hardly any red coloration to phenolphthalein except on dilution with water or on long standing. The fresh solution of the crude bicarbonate filtered in the atmosphere of CO_2 and carefully protected from exposure to the air shows hardly any red coloration with phenolphthalein at first, but red coloration gradually and rapidly develops on standing in contact with the air. Then, when $BaCl_2$ is added to precipitate the carbonate in this solution, the red coloration in the solution again disappears. This shows the absence of any large quantity of normal carbonate, Na_2CO_3, either in the mother liquor or in the precipitate of bicarbonate in the towers. Much of the Na_2CO_3 found in the crude filter bicarbonate is formed during the short exposure to the air during or after filtration.

The complete analysis of the bicarbonate comprises the determination of:

(a) Total Cl
(b) Total NH_3
(c) Fixed NH_3
⌠(d) Total alkalinity
⌡(e) SO_3
(f) Total CO_2
(g) Bicarbonate CO_2
(h) Na_2O
(i) Moisture
(j) Insoluble matter
(k) Fe_2O_3
(l) MgO

For analysis take 10 grams of the crude bicarbonate and dissolve it in cold water to make a volume of 250 cc. in a volumetric flask. Stopper the flask and shake until all has been dissolved except possibly a very small dark residue.

Note.—The sampling of the crude bicarbonate from the filters is one in which it is difficult to get a representative sample as regards the NaCl or moisture content. Where the bicarbonate layer on the filter is heavier and less wash water penetrates through, the per cent NaCl at this spot is apt to show high and the per cent yield low. In practice, a rather large sample from different spots on the filter is taken, from which an average portion is taken for analysis.

(a) **Total Cl.** Pipette 15 cc. of this solution. Exactly neutralize the solution with $6N$ HNO_3 and introduce 0.2 gram $CaCO_3$ (C. P. powder).

Make the volume about 100 cc. and proceed as in (f) under Ammoniated Brine analysis.

(b) **Total NH₃.** Pipette 25 cc. of the solution and determine the total ammonia by distillation as in (e) for fixed NH₃ under Ammoniated Brine analysis.

(c) **Fixed NH₃.** Weigh 3 grams of the crude bicarbonate and suspend it in 100 cc. absolute alcohol. Stir and finally filter by decantation. Repeat once more and wash the residue in the beaker with a little absolute alcohol, filter off and wash again. Evaporate the alcoholic filtrate over a steam bath until about one-third of the original volume is left, or until litmus paper shows no trace of alkalinity. Distill into 50 cc. $N/10$ H_2SO_4 contained in a 150 cc. Erlenmeyer flask with the addition of caustic soda solution as in (e) under Ammoniated Brine analysis. The H_2SO_4 solution from the Erlenmeyer flask is evaporated over a steam bath to drive off most of the alcohol until less than half of the volume is left. Cool and dilute to about 100 cc. and titrate the excess of H_2SO_4 in this solution with $N/10$ NaOH using methyl orange as indicator. Loss in acidity represents fixed ammonia from NH_4Cl.

Note.—Most of the alcohol should be driven off and the solution then diluted with water before titration; otherwise the methyl orange indicator does not give a sharp endpoint in the strong alcoholic solution.

(d) **Total alkalinity.** Pipette 10 cc. of the solution prepared for analysis and titrate with $N/10$ HCl, using methyl orange as the indicator.

(e) **SO₃.** Pipette 50 cc. of the solution, acidify carefully with dilute HCl and add 5 cc. in excess. Bring to a boil and determine SO_3 with $BaCl_2$ as in (g) under Ammoniated Brine analysis.

(f) **Total CO₂.** Pipette 10 cc. of the solution and determine CO_2 as in (i) under Limestone analysis or as in (i) under Ammoniated Brine analysis.

(g) **Bicarbonate CO₂.** Pipette 10 cc of the solution and add 50 cc. $N/10$ NaOH. Add a small excess of neutral $BaCl_2$ solution. Titrate the excess of the NaOH with $N/10$ HCl in the cold, using phenolphthalein as the indicator. Loss in $N/10$ NaOH represents bicarbonate, the CO_2 from which can be deducted from the total CO_2 to give carbonate CO_2.

(h) **Na₂O.** Pipette 15 cc. of the clear portion of the solution into a tared porcelain dish. Acidify carefully with $6N$ HCl, adding a slight excess. Heat to boiling and precipitate the sulfate with a slight excess of $BaCl_2$. Filter, make alkaline with dilute ammonia, and add a slight excess of $(NH_4)_2CO_3$ solution. Heat to boiling and filter. Evaporate the filtrate to dryness and ignite with a low heat until no NH_4Cl fumes are visible. Take up with a little water, transfer to a tared porcelain dish and carefully re-ignite. Cool and weigh the NaCl; whence Na_2O.

For an alternative method, see the triacetate method, p. 505.

(i) **Moisture.** Weigh a 5-gram sample of the crude bicarbonate, spread it in a tared porcelain dish and heat gently, using a heavy sheet of asbestos with a hole cut in the center to project one-third of the dish

below the asbestos board. Finally heat at 300° C. to a constant weight with frequent stirring. Cool and weigh rapidly. The loss in weight less NH_4HCO_3 and NH_4Cl from (b) and (e) and CO_2 and H_2O from the bicarbonate determination in (g) represents moisture.

(j) **Insoluble matter.** The dried sample from the moisture determination is dissolved in about 100 cc. of water. The insoluble residue is filtered off and washed in a tared porcelain filtering crucible. The crucible is dried at 105° C. and the residue represents insoluble matter.

(k) **Fe_2O_3.** The filtrate from the insoluble matter determination is acidified with $6N$ HCl using a slight excess and oxidized with a little bromine. Add 2 grams NH_4Cl. Bring the solution to boiling, and make it slightly alkaline with NH_4OH. Filter off the precipitated $Fe(OH)_3$, ignite and weigh as Fe_2O_3. Or, use standard KCNS solution and compare the color with known standards.

(l) **MgO.** The filtrate from the Fe_2O_3 determination is concentrated to about 75 cc. Determine MgO as in (e) under Brine analysis.

From the above calculate the percentages in the crude bicarbonate of NH_4HCO_3, NH_4Cl, $NaHCO_3$, Na_2CO_3, Fe_2O_3, $MgCO_3$, $NaCl$, Na_2SO_4, free moisture, and insoluble matter.

For control work, it is only required to know the "yield" of the bicarbonate and percentage of NaCl, for which purpose the following method is usually followed in the works laboratory.

Take a 2-gram sample and dry it in a tared porcelain dish by heating to 300° C. with a gentle flame and frequent stirring until the weight is constant. The residue calculated on the percentage basis represents the "yield." This represents the weight of soda ash from the dryers obtainable from the bicarbonate and includes the impurities.

Dissolve the residue in about 100 cc. of water and carefully neutralize with H_2SO_4. Determine the chlorine by Mohr's method according to (f) under Ammoniated Brine analysis. Calculate to NaCl.

The weight of the yield less NaCl can be taken as Na_2CO_3 from which $NaHCO_3$ can be calculated. Subtracting the per cent $NaHCO_3$ and per cent NaCl from 100 gives roughly the per cent free moisture. It will be seen that NH_4HCO_3, NH_4Cl, Na_2SO_4, and insoluble matter ($MgCO_3$, Fe_2O_3, etc.) have been neglected in this control analysis.

The following volumetric method is a more convenient alternative for control work and is no less accurate than the method just described: Weigh a 2-gram sample of the crude bicarbonate as before and dissolve it in about 100 cc. water. Heat the solution in a 250-cc. Erlenmeyer flask and boil until no bubbles of CO_2 are seen in ebullition, or until about half of the volume is left. (The boiling operation is very smooth and requires little attention.) Cool and titrate with N H_2SO_4, using methyl orange as the indicator. The alkalinity calculated as Na_2CO_3 may be taken as the "yield."

After the H_2SO_4 titration, the solution is diluted to about 100 cc. Determine the chlorine as before. Calculate to NaCl. The per cent free

moisture in the bicarbonate may be taken as roughly equal to 100 less the per cent $NaHCO_3$ and per cent NaCl as before.

In both of these control methods, NH_4HCO_3 is decomposed and driven off by heating, and NH_4Cl is converted back to NaCl by $NaHCO_3$ and left as NaCl in the ash or in the solution.

$$NH_4Cl + NaHCO_3 \rightarrow NH_4HCO_3 + NaCl$$
$$NH_4HCO_3 \rightarrow NH_3 + CO_2 + H_2O$$
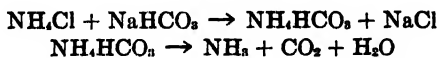
Sampling. Sampling is a very important phase of chemical analysis. The analyses may be made accurately and the results may be good to the fourth significant figure; yet sampling is oftentimes an unknown factor. Frequently, the value of an analysis is impaired because of a question as to correct sampling or as to whether or not the sample is really representative. In the routine analyses on Soda Ash, Caustic Soda, Liquid Caustic, etc., many points need be observed. It is evidently not possible to cover all possible cases in a chapter like this. Suffice it to mention a few observations for some more important products.

A shipment of soda ash, whether in bulk or in gunny bags, should be carefully sampled by taking samples from the outside layer as well as from the interior of the mass. All portions on the surface or in the center, also both in lumps and in loose powder, should be included, and then an average portion be secured by a mechanical sampler. Soda ash is rather susceptible to the action of atmospheric moisture and CO_2, and so care should be taken to avoid unnecessary exposure and to place the sample in a glass-stoppered bottle. As an illustration of a difference in composition between portions of soda ash in the center and on the outer layer in a bag, the reader is referred to p. 510 in the following chapter.

In the case of solid caustic shipped in drums, the mass of the caustic inside an individual drum is generally not homogeneous. In the course of solidification of the molten caustic in the drum, a partial segregation of some of the constituents usually takes place in the center (cone depression) and at the bottom. It is necessary that suitable portions of the caustic from the cone, from the sides, and from the bottom of the drum be included. Caustic soda is more likely to take up CO_2 and moisture from the air and it is exceedingly important that minimum exposure to the air be permitted.

In the case of liquid caustic shipped in tank cars, transportation by rail over territories having sub-zero temperatures usually causes separation from the liquid mass of solid crystals with various degrees of hydration, and consequently a change in composition in the remaining liquid. Samples should be taken only upon complete thawing with steam coils provided in the car, and after complete mixing. Exposure to air causes very rapid absorption of the atmospheric CO_2 and moisture. Hence closed vessels are recommended even during weighing.

In the case of refined sodium bicarbonate, shipment is generally made in paper-lined wooden barrels, or in kegs similarly protected. Because

of its high purity and its use in making drinks, baking powder and pharmaceuticals, shipment in closed containers only is allowed. The fine, loose crystals have a tendency to lose CO_2 upon exposure to the air, and may also become lumpy when in contact with damp atmosphere during storage or transit. Hence sampling must include correct proportions of the outer and inside portions of the mass.

IX. Soda Ash

The use of soda ash as a chemical has long been known. Historically, it is the father of many industries. The test standards for purity are different in different countries. It is sometimes expressed as the per cent Na_2O based on the incorrect atomic weight of sodium of 24 instead of 23, as in the Newcastle test in England. In America the ratio of the incorrect atomic weight of sodium to the correct atomic weight was employed and a system known as the New York and Liverpool test came into use. In Germany and Russia, the tests are reported as per cent Na_2CO_3. In France and Belgium, the degree of purity is figured on the weight of H_2SO_4 necessary to neutralize 100 parts of soda ash (the Descroizilles degree). The available Na_2O based on the correct molecular weight of Na_2O (the Gay-Lussac degree) is becoming more and more widely adopted. It is now customary to regard 99.16 per cent Na_2CO_3 as 58 per cent ash, meaning 58 per cent Na_2O on the correct atomic weight. Not only soda ash but also caustic soda, sodium bicarbonate, and other alkaline products are expressed in these figures. Just how such erroneous calculations based on wrong atomic weight came into use is a matter of historical interest. We shall not discuss it here, except to give the relationship among the various degrees in use in different countries. (See Table 152.) Details are given in Table 163.

Table 152. Comparison of Soda Test Degrees in Different Countries.

Gay-Lussac Na_2O	German Na_2CO_3	Newcastle	New York and Liverpool	Descroizill H_2SO_4
1 or $\dfrac{31}{31}$	$\dfrac{53}{31}$	$\dfrac{31.4}{31}$ $=\dfrac{53}{31}\times\dfrac{32}{54}$	$\dfrac{32}{31}$	$\dfrac{49}{31}$
Thus 58°	99.16°	58.76°	59.87°	91.74°

Soda ash absorbs moisture and CO_2 rapidly. Different samples can only be compared on water-free and bicarbonate-free bases. (See Chapter XXIX.) This is the correct way to judge the purity of a product. Samples received in the laboratory are first calcined and the analysis is then made on the dried ash. Incidentally, this gives the free moisture and the bicarbonate—CO_2 and H_2O in the sample. The complete chemical analysis of soda ash includes:

Chemical Analysis	*Physical Tests*

<div>

Chemical Analysis

  (a) Moisture
  ⌠ (b) SiO$_2$
  ⎮ (c) Fe$_2$O$_3$
  ⎨ (d) CaO
  ⎩ (e) MgO
  ⎰ (f) SO$_3$
  ⎱ (g) Na$_2$O
  ' (h) Bicarbonate
  (i) Carbonate
  (j) Cl

Physical Tests

  (k) Density
  (l) Degree of Fineness
  (m) Clearness of Solution
  (n) Color
  (o) Water Absorbing Power

</div>

Chemical Analysis. Laboratory Method

(a) **Moisture and bicarbonate-H$_2$O and CO$_2$.** Weigh a 10-gram sample and spread it in a tared porcelain dish. Heat to 300° C. to a constant weight as in (i) under Crude Bicarbonate analysis. The loss in weight less bicarbonate-H$_2$O and CO$_2$ represents the free moisture.

(b) **SiO$_2$.** There is practically no silica in the ammonia soda ash. If it is necessary to determine SiO$_2$, dissolve the dried sample from the moisture determination and follow procedure (b) under Limestone analysis.

(c) **Fe$_2$O$_3$.** Dissolve the dried sample in about 100 cc. of water and carefully acidify with 6N HCl. Or, take the filtrate from the SiO$_2$ determination (b). Heat to boiling, add 8 grams NH$_4$Cl and determine Fe$_2$O$_3$ with 6N NH$_4$OH as in (k) under Crude Bicarbonate analysis.

Note.—A very accurate method of determining small amounts of iron is as follows: Take a 10 g. sample and dissolve it by carefully adding a small excess of dil. HCl. Heat the solution to boiling, reduce with SnCl$_2$ solution drop by drop until just barely colorless. Immediately cool in water completely and add an excess of HgCl$_2$ when a silky fibrous precipitate is seen. Add 10 cc. conc. phosphoric acid and titrate with N/10 KMnO$_4$ to a faint purple coloration. This is a modified Zimmermann-Reinhardt method.

Instead of using KMnO$_4$ solution as in the above mentioned Zimmermann-Reinhardt's method, the solution after the addition of the HgCl$_2$ and of phosphoric acid may be titrated with 0.10N K$_2$Cr$_2$O$_7$ solution, using 3 drops of 0.01 molar diphenylamine sodium sulfonate solution as indicator, until a drop of the K$_2$Cr$_2$O$_7$ solution turns the solution reddish violet.

(d) **CaO** and (e) **MgO.** Follow procedures (e) and (f) under Limestone analysis.

(f) **SO$_3$.** Weigh 10 grams of the original sample and dissolve in freshly boiled distilled water to make a volume of 250 cc. in a volumetric flask. Pipette 25 cc. into a 250-cc. beaker. Acidify slowly with 6N HCl, adding 5 cc. in excess and make the volume about 100 cc. Bring to boiling and precipitate the SO$_3$ with a slight excess of N BaCl$_2$. Filter and ignite the precipitate as in (f) under Brine analysis.

(g) **Na$_2$O.** The filtrate from the SO$_3$ determination (f) is concentrated to 15 cc. and neutralized with 6N NH$_4$OH. To the cold solution, add 15 cc. 5N (NH$_4$)$_2$CO$_3$ and 30 cc. 95 per cent alcohol. Stir and set aside for half an hour with frequent stirring. Filter into a 150-cc. cas-

serole and wash with a little $(NH_4)_2CO_3$. Evaporate off the alcohol from the filtrate over the steam bath and ignite off $(NH_4)_2CO_3$ and NH_4Cl. Dissolve in a little water and transfer to a tared porcelain dish. Evaporate and ignite again, avoiding intense heat. Cool and weigh the NaCl; whence Na_2O.

(h) **Bicarbonate** * and (i) **Carbonate.** Pipette into a 100-cc. beaker 10 cc. of the clear portion of the solution made for SO_3 determination (f), dilute to 50 cc., add 5 grams C. P. NaCl and cool in ice water. Add 2 or 3 drops of phenolphthalein and titrate the solution with $N/10$ HCl, keeping the tip of the burette under the solution and moving the glass rod very gently. The end point is reached when the red color just disappears. Add a drop of methyl orange, lift the burette tip out of the solution, and continue the titration until the slight yellow color changes to pink.

Note.—This double indicator method does not give a very sharp endpoint with phenolphthalein, the red color of which disappears only gradually in the presence of a large amount of $NaHCO_3$ in solution. With a little practice, Sundström's method for determining bicarbonate in the presence of a large amount of carbonate (such as in soda ash) is both convenient and accurate.

Bicarbonate CO_2 (alternative method, Sundström). Pipette 10 cc. of the solution and dilute to about 50 cc. Titrate it with $N/10$ NaOH, using 10 per cent $AgNO_3$ solution as an outside indicator on a spot plate. A white precipitate of Ag_2CO_3 or $AgHCO_3$ is seen. The end point is registered by observing the slight dark color in the white precipitate formed immediately and not on long standing. This value, when deducted from the total alkalinity determined by titration with an acid using methyl orange as the indicator, gives the carbonate.

(j) **Cl.** Pipette 10 cc. of the solution made for SO_3 determination (f) and neutralize carefully with $6N$ H_2SO_4. Add 0.2 gram C. P. $CaCO_3$. Stir and dilute to about 100 cc. Titrate the chloride with $N/10$ $AgNO_3$, using 15 per cent K_2CrO_4 solution as the indicator as in (f) under Ammoniated Brine analysis.

Physical tests

(k) **Density.** This is the apparent density, *i.e.*, the bulk weight of soda ash contained in a given unit of volume. It is expressed in grams per liter or pounds per cubic foot. It expresses the bulkiness of soda ash. Then again density depends upon how closely the ash is packed. In practice the two extremes are taken—one is the weight when tightly packed or tapped until no further shrinkage in volume is observed, and the other is the weight when loosely packed, avoiding any exertion of pressure. The difference between the two is as follows: The light ash, when tightly packed until no further shrinkage is observed, occupies a volume only 63 per cent as great as when loosely packed. The density figures thus depend greatly upon how the density is taken. The following table shows average figures for densities of various grades of soda ash by the two methods. The second method, however, is the one that is now generally

* *Cf.* Lunge and Keane, "Technical Methods of Chemical Analysis," Vol. 1, Part 1, p. 469.

adopted, as it shows more nearly the space required by a consignment of soda ash during transportation or storage. (See Table 153.)

TABLE 153. Average Densities of Various Grades of Soda Ash by the Two Methods.

Grade	Tightly Packed Grams/1000 cc.	Loosely Packed Grams/1000 cc.	Loosely Packed Lbs./cu. ft.
Extra light ash	550	370	23
Light ash	900	550	34
Medium ash	1150	800	50
Heavy ash	1500	1050	66

In the laboratory the method of determination depends, of course, upon the system chosen. If the loosely packed system is adopted, the procedure is to fill a known volume of a tared container (say a brass cylinder of exactly 500 cc. capacity), with a sample of soda ash, level
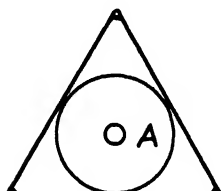
FIG. 127.

Apparatus for density determination by loosely packed method.

A is a funnel of somewhat larger than 500 cc. capacity.

B is a flap cover with a spring hinge.

C is a brass cylinder, 7 cm. inside diameter, made of 2½ inches of brass pipe, having a volume of exactly 500 cc.
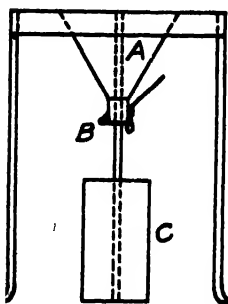
the top off without exerting any pressure, and weigh again. The number of grams of contents times two is the density sought. The apparatus is arranged as in Fig. 127.

Procedure: Fill the funnel *A* with the ash. Tip the flap cover *B* to allow the ash to flow into the cylinder *C* below. With a large steel spatula, level off the top of the cylinder and weigh the content. The weight less the tare times two is the density of the ash in grams per liter or kilos per cubic meter.

(1) **Fineness.** Weigh 100-grams of the sample and put it through an 8-mesh screen. Weigh the portion that passes through the screen and

the portion left on the screen. From the portion that passes through the 8-mesh screen, determine the quantity that passes through a 12-mesh screen and that which is left on the 12-mesh screen. Repeat with 16-mesh screen, etc. The ash that is fresh from the dryers and that has not been weathered will all pass through an 8-mesh screen. If it has been kept in storage or has taken up moisture during transportation, large lumps may be formed. The screen analysis is either "differential" or "cumulative" according to whether the result is expressed as the percentage retained by each individual screen or as the total percentage retained by all screens up to a particular mesh.

(m) **Clearness of solution.** This registers the amount of insoluble matter or "mud" in the ash in a qualitative way and is generally due to the presence of $MgCO_3$. For determination, take 15 grams of the sample and dissolve it in 100 cc. of water. Compare the turbidity of the solution with known standards. Good ash should contain very little insoluble matter and the solution should be practically clear and free from cloudy precipitate. At the bottom of the solution there should not be present any red or dark particles. Magnesium that has not been completely separated out as mud from ammoniated brine will cause cloudiness or even precipitate in the solution.

(n) **Color.** Good ash should be perfectly white. The presence of iron will cause red color in the ash. Frequently iron is present as isolated red particles in the ash which are detectable even by the naked eye. Good-colored ash should not appear yellowish at all when a solution is made as in (m). The most severe test is to take 50 grams of the ash and macerate it with just sufficient water to form a thick paste. Any color in the ash will show in an exaggerated degree in the paste form. Light ash carries not more than 0.003 per cent Fe_2O_3. Dense ash may carry a little higher (0.004 to 0.005 per cent).

(o) **Water-absorbing power.** This test is sometimes made when the ash is to be made into blocks. The water absorbing power is the maximum quantity of water that the ash will take before the paste fails to set to a firm solid block on cooling. For testing, 100 grams of the ash is taken, placed in a mortar and ground with the desired amount of water. During the course of continued grinding, the thin solution gradually thickens; and when the thickened paste is poured into a mold, it should set or solidify to a firm block on cooling. The water-absorbing power depends on (1) the purity of the ash (*i.e.*, per cent Na_2CO_3 not including $NaHCO_3$), (2) the freshness of the product, *i.e.*, how far it has been weathered or how much moisture and CO_2 it has taken from the atmosphere, and (3) the weather conditions, *i.e.*, in winter or in summer seasons. In winter, good fresh ash will take as much as 135 per cent water on the weight of the ash, but in summer 110-120 per cent water may be the maximum.

For routine analysis in ammonia soda plants only the following determinations are required:

    (a) Moisture
  { (b) Insoluble matter
  { (c) Available Na_2O
    (d) $NaHCO_3$
    (e) NaCl
    (f) Na_2SO_4
    (g) Fe_2O_3
    (h) Density

In the works, moisture is not determined because fresh ash immediately after it comes from the dryers contains no water.

(b) **Insoluble matter.** Weigh 10 grams of the sample and dissolve in 200 cc. of water in a 350-cc. beaker. Bring the solution to a boil and filter through a tared filtering crucible and receive the filtrate in a 350-cc. beaker. Wash thoroughly with hot water. Dry the crucible at 105° C. The residue is insoluble matter.

(c) **Available Na_2O.** Cool the filtrate from above and make the volume 500 cc. Pipette 10 cc. and titrate with $N/10$HCl, using a drop of methyl orange as indicator.

(d) **$NaHCO_3$ (Sundström's method).** Pipette 10 cc. of the solution. Dilute it to 100 cc. Titrate with $N/10$ NaOH, using 10 per cent $AgNO_3$ solution on a spot plate as an outside indicator. A drop of the solution from the glass rod giving an immediate brownish cast in the bluish-white precipitate with $AgNO_3$ solution on the spot plate registers the endpoint.

(e) **NaCl.** Pipette 10 cc., neutralize with dilute H_2SO_4 and dilute to 100 cc. Add 0.2 gram C. P. $CaCO_3$. Determine chlorine by Mohr's method as in (f) under Ammoniated Brine analysis.

(f) **Na_2SO_4.** Pipette 100 cc. and neutralize carefully with $6N$ HCl, adding 5 cc. in excess as in (g) under Ammoniated Brine analysis. Calculate as Na_2SO_4.

(g) **Fe_2O_3.** Weigh a 2-gram sample and dissolve it in about 50 cc. of water. Add a slight excess of $6N$ HCl. Bring to a boil, filter if there is any residue, make the solution slightly alkaline with $6N$ NH_4OH, and determine iron as in (k) under Crude Bicarbonate analysis. When the quantity of iron in the ash is very small, a better way is to make the volume of the acidified solution 100 cc. and place it in a Nessler tube. Add 2 cc. 10 per cent KCNS solution and determine the per cent Fe_2O_3 by comparing with known standards made in the same way.

(h) **Density.** This is determined by one of the two ways described above, according to which system is adopted.

For control work in the field, when the per cent Na_2CO_3 and per cent ·NaCl are to be determined, take 2.65 grams of the sample by placing this fixed weight on the scale pan, dissolve the soda ash in about 25 cc. water and titrate the solution with N H_2SO_4 solution, using methyl orange as the indicator. Twice the number of cc. of the N H_2SO_4 used is the per cent Na_2CO_3 in the ash. The same solution then is titrated

with 0.453 N AgNO$_3$ solution as in (f) under Ammoniated Brine analysis. The number of cc. of the AgNO$_3$ used is the per cent NaCl in the soda ash.

X. Distiller Waste Liquor

The distiller run-off liquor affords an index to the efficiency of the whole process. From the composition of the liquor may be calculated (1) the utilization of NaCl in the brine, (2) the utilization of lime in the distiller operation, (3) the loss of NH$_3$ in the distiller, (4) the volume of brine, of distiller waste, etc., per ton of soda ash made, etc. The concentration of distiller waste and consequently its specific gravity vary a great deal, depending upon the efficiency of operation and the dilution of the mother liquor by filter wash water, steam condensate, and various ammonia-bearing liquors at different stages. For complete analysis the following determinations are required:

> (a) Specific gravity and temperature
> (b) Total NH$_3$
> (c) Excess CaO
> (d) Total CO$_2$
> (e) Total Cl
> (f) SiO$_2$ and silicious matter ⎤
> (g) Fe$_2$O$_3$, Al$_2$O$_3$, etc. ⎟
> (h) CaO ⎟
> (i) MgO ⎬ in one portion.
> (j) Na$_2$O ⎟
> (k) SO$_3$ ⎦

(a) **Specific gravity and temperature.** Determine the specific gravity of the cold sample with a hydrometer by stirring the suspension with a thermometer. Note the temperature at the same time.

(b) **Total NH$_3$.** Pipette 50 cc. of the sample into a 250-cc. distilling flask, using a pipette having a large bore in the tip. Dilute to 75 cc. Determine ammonia by distillation in the usual way, adding NaOH if necessary.

(c) **Excess CaO.** Pipette 100 cc. of the sample and dilute to 500 cc. in a volumetric flask. Pipette 10 cc. of the suspension with a pipette having a large bore tip. Boil off any ammonia and then dilute to about 50 cc. Titrate with $N/10$ HCl, using phenolphthalein as the indicator. Take the end point when the red color first disappears.

An alternative method for the determination of the excess CaO approximating the condition in the distiller is as follows: Pipette off 10 cc. of the well-shaken suspension as before, boil off ammonia and place it in a 150-cc. distilling flask, adding a small excess of neutral (NH$_4$)$_2$SO$_4$ solution. Distill NH$_3$ into the H$_2$SO$_4$ solution, proceeding exactly in the same way as in the Fixed Ammonia determination.

(d) **Total CO$_2$.** Pipette 10 cc. of the suspension and determine CO$_2$ as in (i) under Ammoniated Brine analysis.

(e) **Total Cl.** Pipette 10 cc. of the suspension made in (c) and neutralize with dilute HNO_3 free from chlorides. Add 0.2 gram C. P. $CaCO_3$ and dilute to about 100 cc. Titrate with $N/10$ $AgNO_3$ solution, using 15 per cent K_2CrO_4 as the indicator in the usual way.

(f) **SiO_2 and silicious matter.** Pipette 10 cc. of the original sample. Acidify with $6N$ HCl and determine SiO_2 as in (b) under Limestone analysis.

(g) **Fe_2O_3, Al_2O_3, etc.** Determine the combined oxides in the filtrate from (f) above as in (d) under Limestone analysis.

(h) **CaO.** Determine CaO in the filtrate from the Combined Oxide determination (g) as in (e) under Limestone analysis.

(i) **MgO and** (j) **Na_2O.** The filtrate from the CaO determination is acidified with an excess of $6N$ H_2SO_4, and ignited in a casserole until no dense fumes of SO_3 come off. It is cooled completely, taken up with a little water, and transferred to a tared porcelain dish. It is then evaporated to dryness and ignited as before. The residue is weighed as Na_2SO_4 and $MgSO_4$.

The combined sulfates are dissolved in 75 cc. of water in a 250-cc. beaker. MgO is determined with Na_2HPO_4 in the usual way.

The weight of combined sulfates less $MgSO_4$ from $Mg_2P_2O_7$ gives Na_2SO_4, from which Na_2O is calculated.

(k) **SO_3.** Pipette 25 cc. of the diluted suspension made in (c) above, acidify with $6N$ HCl, adding 5 cc. in excess. Dilute to about 100 cc. Bring to a boil and filter. Determine SO_3 in the filtrate with $BaCl_2$ in the usual manner.

For routine analysis in the plant, only the following are determined:

(a) Specific gravity and temperature
(b) Excess CaO
(c) Total NH_3
(d) Total Cl

This last item (total chlorine) is determined in order to estimate the degree of dilution and the volume of distiller waste per ton of soda ash made.

XI. Heater Liquor

This is the sample of the liquor from the bottom of the heater which enters the prelimeing tank or lime still before adding lime. It should be analyzed for CO_2 in accordance with (i) under Ammoniated Brine analysis. This analysis should be made in the field as well as in the laboratory to determine the work of the heater so as to guide the distiller operation. The excessive amount of CO_2 left in the heater liquor causes a loss of available lime in the lime still or in the prelimer.

The distiller feed liquor is essentially the tower draw liquor and can be analyzed in the same way as the latter. Comparison of chlorine con-

centrations in the distiller feed liquor and in the heater liquor will show dilution by steam condensate in the heater. Comparison of chlorine concentrations in the mother liquor and in the distiller waste, neglecting a small amount of NaCl present in the liquor from "mud" pumped into the top of the heater, will show the volume of the distiller waste per ton of soda ash. The volume of milk of lime required per ton of soda ash can be estimated from the fixed NH_3 present in the distiller feed liquor (considering the excess CaO left in the distiller waste) and the volume of the distiller feed liquor per ton of soda ash. Finally, from the volume of the heater liquor, of milk of lime, and of the distiller waste per ton of soda ash, the volume of steam condensate in the lime still can be estimated.

To check up possible leakages in the cooling tubes in all coolers, condensers, preheaters, etc., the exit cooling water and sewer waste should be occasionally tested with Nessler's reagent; and, if ammonia is found present, the leakage should be traced and immediately attended to. Wherever possible, arrangement should be made so that the cooling water at the exit is under a slight pressure so that, should any leakage occur, it is the water that goes into the apparatus.

II. Bicarbonate Manufacture

For methods of analysis of solutions used in the bicarbonate manufacture the procedures given under the soda ash process are applicable. They will not be repeated here. The soda liquor can be analyzed like any other Na_2CO_3 solutions with tests for the specific gravity and temperature. The refined bicarbonate in the bicarbonate process can be analyzed in the same way as the crude bicarbonate from the filters in the soda ash process with the omission of the ammonia determinations. The yield of bicarbonate from the filters or from the centrifuges is determined also in the same way. However, the product here is of higher purity than that from the soda ash process.

III. Chemical Caustic Manufacture

Caustic soda in the ammonia soda works is produced by the so-called chemical process, *i.e.*, by causticization with lime. This can produce a caustic of equal or higher purity than the electrolytic process, because the raw material used (*i.e.*, Na_2CO_3) to start with has a high purity. This lime process furnishes roughly one-half of the total caustic soda made in the United States, the remaining half being supplied by the electrolytic process.

XII. Caustic Liquors

These are liquors either from the causticization tanks or at different stages of concentration. They are called weak or strong liquors according to their relative strengths. They are analyzed in the laboratory for:

(a) Specific gravity and temperature

{
(b) Total alkalinity
(c) Na₂CO₃
(d) NaCl
}

(e) Na₂SO₄

(a) **Specific gravity and temperature.** These are taken with a hydrometer and a thermometer as described previously.

(b) **Total alkalinity**
(c) **Na₂CO₃** }. Pipette 25 cc. of the sample and make the volume 250 cc. in a flask. Take 10 cc. of the diluted solution and titrate with $N/10$ H_2SO_4 using phenolphthalein as indicator. Note the reading. Add a single drop of methyl orange and continue the titration until the slight yellowish color changes to pink. The methyl orange endpoint gives the total alkalinity. Calculate as per cent Na_2O. Twice the difference between the methyl orange reading and the phenolphthalein reading represents Na_2CO_3.

(d) **NaCl.** The solution from methyl orange titration can be further analyzed for chlorine by adding 0.2 gram $CaCO_3$ and titrating with $N/10$ $AgNo_3$ with 15 per cent K_2CrO_4 indicator in the usual way. Calculate to NaCl.

(e) **Na₂SO₄.** Pipette 25 cc. of the solution made in (b) and (c) above, acidify with $6N$ HCl and determine SO_4^{--} with $BaCl_2$ in the usual way. Calculate to Na_2SO_4.

In the causticizing room for control work, the specific gravity of the liquor and the per cent conversion only are required. The latter is determined by the double indicator titration as above and the per cent conversion is obtained by reference to a chart or table prepared for this purpose.

$$\% \text{ conversion} = \frac{\text{Methyl orange reading} - 2 \times \text{diff. in the two readings}}{\text{Methyl orange reading}} \times 100$$

XIIA. Caustic Liquor. Rapid Method.

This is a sample of the liquor being causticized and is taken from the causticizing tanks. It is analyzed for the excess of lime and per cent conversion. The following is a rapid method for control work in the field.

(a) Per cent NaOH
(b) Per cent Na₂CO₃
(c) Per cent Conversion } in one sample
(d) Per cent Excess lime

(a) **NaOH** and (b) **Na₂CO₃.** Pipette 5 cc. of the suspension, using a pipette with a large bore at the tip, and deliver onto a small filter paper on a porcelain suction filter. Apply suction and wash the residue rapidly with a little distilled water. Titrate the filtrate in the suction flask with $N/2$ HCl, first using phenolphthalein and then methyl orange. The phenolphthalein reading less the difference between the methyl orange

reading and the phenolphthalein reading represents NaOH. Twice the difference between the phenolphthalein reading and the methyl orange reading represents Na_2CO_3.

(c) **Per cent conversion** $= 100 \times \dfrac{NaOH}{NaOH + Na_2CO_3}$

(d) **Excess lime.** Suspend the residue from the filter above in 100 cc. of distilled water in a 250-cc. beaker, taking with it the filter paper. Titrate the suspension with $N/2$ HCl, using phenolphthalein as indicator. This represents excess lime.

XIII. Caustic Mud

Caustic mud is the sludge from the causticization tanks containing precipitated calcium carbonate, excess lime, soluble alkalies and all the impurities in the lime. This is analyzed in the laboratory for:

$\left\{\begin{array}{l}\text{(a) Total alkali} \\ \text{(b) Caustic lime, CaO} \\ \text{(c) } CaCO_3\end{array}\right.$
(d) Moisture

(a) **Total alkali and** (b) **Caustic lime.** Take a 5-gram sample and suspend it in about 150 cc. of water with constant stirring. Titrate the suspension with $N/2$ HCl solution, using phenolphthalein as the indicator. This gives the total alkali and $Ca(OH)_2$. Filter and wash the residue by decantation. Determine calcium in the combined filtrate by precipitating it with $(NH_4)_2C_2O_4$, and subtract the CaO so found from the figure obtained by the above titration. This gives the total alkali, and the calcium determination gives caustic lime.

(c) **$CaCO_3$.** Suspend the residue from the above HCl titration in about 100 cc. of water. Titrate the suspension with $N/2$ HCl solution, using methyl orange as the indicator. Or, suspend the residue in about 100 cc. of water and add a small excess of a known amount of $N/2$ H_2SO_4. Boil off CO_2 and titrate back with $N/10$ NaOH solution, using methyl orange as the indicator. This gives $CaCO_3$.

Two alternative methods for the total alkali determination are given below:

(a) **Total alkali.** Leach a 25-gram sample of the sludge with about 50 cc. of hot water, allow to settle and decant the clear solution. Repeat with another 50 cc. of hot water. Finally add about 75 cc. of water, heat carefully, filter, and wash. To the combined filtrates, pass in CO_2 gas for 10 minutes. Allow to settle and filter by decantation. Titrate the filtrate with $N/10$ HCl, using methyl orange as the indicator.

The other method is as follows:

(b) **Total alkali.** Weigh a 5-gram sample of the caustic sludge into a 250-cc. casserole. Cover with about 25 cc. of water and stir. Add 10 cc. 5N $(NH_4)_2CO_3$ solution, stir, and evaporate just to dryness over a steam bath. Break up the residue in the casserole and repeat by adding another

10 cc. $5N$ $(NH_4)_2CO_3$ solution. Add 75 cc. of water and heat to boiling. Filter by decantation, washing the residue thoroughly. Titrate the Na_2CO_3 in the filtrate with $N/10$ HCl solution, using methyl orange as the indicator.

(d) **Moisture.** Weigh 5 g sample of the mud and dry it in an electric oven at 105° C. to a constant weight. The loss in weight gives approximately water in the mud, neglecting the small amount of CO_2 that may be picked up by NaOH during drying.

In the causticizing room the amount of alkalies left in the mud is regulated by the extent and efficiency of washing. This amount should be very small when mechanical washing equipment is employed, such as a Dorr thickener.

XIV. Caustic Salts (Fished Salts)

These are crystals of NaCl, Na_2CO_3, or Na_2SO_4 together with hydrates of NaOH separating out from strong caustic liquor during or after evaporation on cooling. They are analyzed for:

$$\begin{cases} \text{(a)} & NaOH \\ \text{(b)} & Na_2CO_3 \\ \text{(c)} & NaCl \\ \text{(d)} & Na_2SO_4 \end{cases}$$

For analysis, weigh 20 grams of the sample and make the volume of the solution 500 cc. in a volumetric flask.

(a) **NaOH and** (b) **Na_2CO_3.** These are determined by the double indicator method in the usual way, using $N/10$ H_2SO_4.

(c) **NaCl.** To the solution after total alkali titration add 0.2 gram C. P. $CaCO_3$ and titrate with $N/10$ $AgNO_3$, using 3 drops of 15 per cent K_2CrO_4 as indicator.

(d) **Na_2SO_4.** Pipette 25 cc. and acidify with $6N$ HCl adding 5 cc. in excess. Heat to boiling and determine SO_3 with $BaCl_2$ in the usual way. Calculate to Na_2SO_4.

XV. Solid Caustic and Liquid Caustic.

Liquid caustic is getting to be one of the standard products in commerce. Samples of solid caustic from caustic pots (76 per cent Na_2O) or liquid caustic of 48° to 50° Bé. from evaporators are analyzed for:

(a) Total alkali	(d) Na_2CO_3
(b) NaCl	(e) Na_2SO_4
(c) NaOH	(f) H_2O

Weigh quickly a 10-gram sample of the solid caustic and make the volume of the solution 500 cc. in a volumetric flask.

(a) **Total alkali.** Pipette 10 cc. of the solution and titrate with $N/10$ H_2SO_4, using methyl orange as the indicator. Calculate to Na_2O.

(b) **NaCl.** The solution from the total alkali determination is

titrated with $N/10$ AgNO$_3$ for chlorine as in (c) under Caustic Salts (Fished Salts) analysis. Calculate to NaCl.

(c) **NaOH.** Pipette 10 cc. of the solution, add 10 cc. N BaCl$_2$ and titrate with $N/10$ HCl, using phenolphthalein as the indicator.

(d) **Na$_2$CO$_3$.** The difference between the total alkali and NaOH gives Na$_2$CO$_3$.

(e) **Na$_2$SO$_4$.** Pipette 50 cc. of the solution and determine Na$_2$SO$_4$ as in (d) under Fished Salts analysis.

(f) **Water.** Water is usually formed by deducting the percentages of NaOH, Na$_2$CO$_3$, NaCl, and Na$_2$SO$_4$ from 100.

XVA. Solid Caustic or Liquid Caustic. Laboratory Method

If SiO$_2$, Fe$_2$O$_3$, Mn and Cu in the solid or liquid caustic are to be determined, weigh a 10 g. sample of the solid caustic or 20 g. sample of liquid caustic and make the volume of the solution 500 cc. in a volumetric flask.

(a) **SiO$_2$.** Pipette 25 cc. of the solution into a 200 cc. casserole, acidify with $6N$ HCl and determine SiO$_2$ by double dehydration as in (b) under IIIA, Limestone analysis.

(b) **Fe$_2$O$_3$.** Pipette 50 cc. of the solution made above in a 250 cc. beaker, acidify with $6N$ HCl and determine iron as in (c) under Chemical Analysis for Soda Ash, Laboratory Method (p. 484).

(c) **Mn.** Weigh a 5 g. sample of solid caustic or 10 g. sample of 50 per cent liquid caustic and dissolve it in 50 cc. water in a 200 cc. casserole. Acidify by adding 20 cc. $6N$ H$_2$SO$_4$ and 5 cc. of 70 per cent HClO$_4$ solution. Evaporate until copious fumes of SO$_3$ are evolved, continually whirling the solution over a small flame. Cool completely and add cautiously 30 cc. distilled water. Filter off SiO$_2$ through a No. 44 Whatman filter paper, washing the residue with hot water. Make the volume of the filtrate about 90 cc., add 2 cc. 85 per cent H$_3$PO$_4$ and 0.5 g. KIO$_4$. Boil gently for 15 min. Cool the solution, transfer it to a clean Nessler tube and make up to the 100 cc. mark with $2N$ H$_2$SO$_4$ which has previously been boiled with a little KIO$_4$.

Prepare KMnO solution standards in a series of Nessler tubes as in the test sample, using known strengths of KMnO$_4$ and the same concentrations of H$_2$SO$_4$ and H$_3$PO$_4$. Compare the sample solution with these standards and determine per cent Mn in the caustic soda sample by matching the color of the solution.

(d) **Cu** (Modified Low's Method). Weigh the same size sample as in (c) and acidify with $6N$ H$_2$SO$_4$. Heat the solution to boiling, add 20 cc. 10 per cent sodium thiosulfate solution (see Note below), and continue boiling for about $\frac{1}{2}$ hour. Filter on suction filter and wash several times with hot water. Ignite the residue on a porcelain crucible, take up with a little conc. HNO$_3$ and ignite gently until nitric acid is all expelled and copper oxide remains. Dissolve the copper oxide with a small amount of $6N$ H$_2$SO$_4$ with heating, and transfer the solution to a 250 cc. Erlenmeyer flask. Neutralize with dilute Na$_2$CO$_3$ solution until

basic cupric carbonate precipitate persists on shaking. Acidify with dilute acetic acid, cool and add 10 cc. 25 per cent KI solution. Titrate the iodine liberated with $0.10N$ sodium thiosulfate solution, using starch as the indicator in the usual way. (Note: If the caustic contains much Fe_2O_3, Na_2MnO_4 or $NaClO_3$, sufficient sodium thiosulfate must be added to reduce these oxidizing impurities before copper is precipitated.)

XVI. Caustic "Bottoms"

They are analyzed in the same way as above but in addition Fe_2O_3, etc. determinations must be made.

XVII. Fused Calcium Chloride (Anhydrous 95 per cent Calcium Chloride) and Liquid Calcium Chloride

These are products from the distiller waste and are analyzed for:

(a) Total chlorine, Cl⁻   (d) $CaCl_2$
(b) $Ca(OH)_2$ in fused (95%) $CaCl_2$ (e) $NaCl$
(c) $CaSO_4$ (f) Water or moisture

Weigh rapidly 10 grams of 95 per cent $CaCl_2$ in a covered weighing tube and dissolve it in water, making the volume 250 cc. in a volumetric flask. In the case of liquid calcium chloride, weigh or pipette an equivalent amount and make up to this volume.

(a) **Total Chlorine, Cl⁻.** Pipette 10 cc. of the solution, neutralize if necessary with a little dilute HNO_3, add a little C. P. $CaCO_3$ powder and titrate with $N/10$ $AgNO_3$, using 3 drops of 15 per cent K_2CrO_4 indicator in the usual way.

(b) $Ca(OH)_2$. In the case of fused (95 per cent) $CaCl_2$, pipette 20 cc. of the above solution, and titrate with $N/10$ HCl, using phenolphthalein as the indicator. Calculate to $Ca(OH)_2$.

(c) $CaSO_4$. Pipette 50 cc. of the above solution, add about 100 cc. of water, acidify with dilute HCl, bring to a boil, and precipitate $BaSO_4$ in the usual way. Ignite with moderate heat and calculate to $CaSO_4$.

(d) $CaCl_2$. Pipette 20 cc. of the dilute solution, add 100 cc. of water and 5 cc. dilute ammonia, heat to boiling and precipitate CaC_2O_4 with $(NH_4)_2C_2O_4$ in the usual way. Deduct from the total calcium found the calcium determined in (b) and (c), and calculate the balance to $CaCl_2$.

(e) **NaCl.** Deduct from the total chlorine found in (a) the chlorine corresponding to $CaCl_2$ in (d) and calculate the balance to $NaCl$.

(f) H_2O. This can be found by difference.

IV. Electrolytic Caustic and Bleach Manufacture

XVIII. Cell Effluent or Weak Liquor

This liquor is analyzed for (a) NaOH and (b) NaCl. If other elements are to be determined, follow the procedure under Brine analysis.

(a) $NaOH + Na_2CO_3$. Take 10 cc. of the sample and make up to 250 cc. in a volumetric flask. Pipette 10 cc. of the dilute solution into a

250 cc. beaker and add 10 cc. neutral H_2O_2 to decompose the hypochlorite. Heat to boiling to decompose excess H_2O_2. Cool and titrate with $N/10$ HNO_3 solution, using methyl orange as the indicator.

(b) **NaCl.** After the NaOH determination, the same solution may be used for the NaCl determination by diluting it to about 75 cc. and adding about 0.2 g. C. P. $CaCO_3$ powder. Stir, and determine chlorine by Mohr's method in the usual manner.

An alternative method of determining chlorine capable of somewhat greater accuracy is as follows: Pipette 10 cc. of the dilute solution and neutralize with $6N$ HNO_3. Add an excess of $N/10$ $AgNO_3$ and titrate with $N/10$ KCNS solution, using 2 to 3 drops of saturated ferric ammonium sulfate solution as the indicator.

(c) **CO_2.** Pipette 10 cc. of the diluted solution and add 5 cc. neutral N $BaCl_2$ solution. Stir and titrate the NaOH, using phenolphthalein as the indicator. Subtracting this result from (a) $NaOH + Na_2CO_3$ gives Na_2CO_3, whence CO_2 in the cell effluent may be calculated.

Table 154 is useful for reference work in the electrolytic caustic plant laboratory.

TABLE 154. Properties of Electrolytic Caustic Solutions.*

NaOH by Wt. %	Sp. Gr. 60°/4°	NaCl by Wt. %	NaCl per 100 Pts. NaOH	H₂O per 100 Pts. NaOH	NaOH by Wt. %	Sp. Gr. 60°/4°	NaCl by Wt. %	NaCl per 100 Pts. NaOH	H₂O per 100 Pts. NaOH
			At 60° C.					At 100° C.	
0	1.187	27.0	......	......	0	1.170	28.20	......	......
2	1.195	25.3	1,265.00	3.635.	2	1.177	26.54	1,327.	3,573.
4	1.202	23.61	590.24	1.810.	4	1.185	24.88	622.	1,778.
6	1.210	21.94	365.66	1,201.	6	1.193	23.20	386.66	1,180.
8	1.219	20.27	253.37	896.62	8	1.201	21.52	268.99	881.
10	1.228	18.70	187.00	712.91	10	1.210	19.96	199.59	700.
12	1.237	17.13	142.75	590.59	12	1.219	18.40	154.85	580.
14	1.246	15.61	111.49	503.07	14	1.229	16.89	120.70	493.50
16	1.256	14.09	88.06	437.43	16	1.238	15.38	96.12	428.87
18	1.266	12.60	70.00	385.77	18	1.248	13.90	77.22	378.33
20	1.277	11.11	55.54	344.45	20	1.259	12.42	62.10	337.90
22	1.287	9.76	44.40	310.60	22	1.269	11.08	50.36	304.18
24	1.299	8.42	35.08	281.58	24	1.280	9.75	40.62	276.04
26	1.312	7.20	27.39	256.89	26	1.292	8.54	32.84	251.76
28	1.325	5.98	21.30	234.67	28	1.305	7.33	26.18	230.93
30	1.338	4.97	16.56	217.26	30	1.318	6.34	21.13	212.20
32	1.352	3.97	12.40	200.09	32	1.332	5.35	16.71	195.78
34	1.367	3.37	9.91	184.20	34	1.347	4.76	14.00	180.11
36	1.384	2.77	7.51	170.08	36	1.363	4.17	11.59	166.19
38	1.401	2.46	6.47	156.68	38	1.380	3.87	10.18	152.09
40	1.419	2.15	5.37	144.45	40	1.398	3.57	8.92	141.25
42	1.437	1.98	4.71	133.38	42	1.417	3.41	8.12	129.97
44	1.457	1.81	4.11	123.16	44	1.435	3.26	7.40	119.86
46	1.476	1.74	3.77	113.60	46	1.454	3.20	6.95	110.43
48	1.496	1.67	3.48	104.85	48	1.473	3.14	6.55	102.07
50	1.516	1.64	3.28	96.72	50	1.493	3.12	6.24	93.76
52	1.536	1.61	3.11	89.19	52	1.513	3.07	5.90	86.38
54	1.557	1.59	2.96	82.44	54	1.534	3.04	5.62	79.50
56	1.578	1.57	2.81	75.75	56	1.555	2.99	5.35	73.22
58	1.601	1.55	2.66	69.73	58	1.576	2.95	5.09	67.31
60	1.624	1.53	2.55	63.11	60	1.600	2.91	4.85	61.81

* Hooker, *Trans. Am. Inst. Chem. Engrs.*, **13**, 1 (1920).

XIX. Bleaching Powder and Bleach Liquor

The bleaching powder is sampled from drums or barrels by means of a sample tube 3 feet long made of $\frac{3}{4}$-inch brass pipe with the end beveled to form a scoop. The pipe is driven into the mass at different places and the composite sample quartered down to laboratory size. For analysis, weigh 7.092 grams and suspend them in a liter of water in a liter volumetric flask. Shake and pipette 25 cc. of the suspension. Follow procedure (b) below. With this size of sample and $N/10$ standard solutions, twice the number of cc. of the reducing solution used represents the percentage of available chlorine in the bleaching powder.

In the case of a bleach liquor, pipette 25 cc. of the liquor and make up to 250 cc. in a volumetric flask. Pipette 25 cc. of this suspension for analysis.

Each of the above samples may be analyzed for (a) free lime and (b) available chlorine.

(a) **Free lime.** Pipette 25 cc. of the dilute suspension. Add neutral H_2O_2 solution to decompose the bleach until the bubbling ceases. Titrate with $N/10$ HNO_3, using phenolphthalein as the indicator.

(b) **Available Chlorine** (Pontius' Method). Pipette 25 cc. of the diluted suspension into a 250-cc. Erlenmeyer flask and dilute to about 75 cc. Add 3 g. $NaHCO_3$ and titrate with $0.10N$ KI solution, adding a little starch as the indicator. The end point is reached when one drop of the KI solution turns the solution blue. Twice the number of cc. of KI solution used represents per cent available chlorine.

(1) $3CaOCl_2 + 6NaHCO_3 + KI \rightarrow 3CaCO_3 + 6NaCl + KIO_3 + 3H_2O + 3CO_2$

(2) $KIO_3 + 5KI + 6CO_2 + 3H_2O \rightarrow 3I_2 + 6KHCO_3$
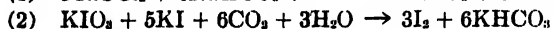
Note that in the above titration $0.10N$ KI solution contains only $1/60$ mol KI per liter.

XIXA. Bleaching Powder or Liquid Bleach. Laboratory Method

"Chloride of lime" is represented by the formula $CaOCl \cdot Cl \cdot H_2O$, in which the theoretical percentage of chlorine is 49. Commercial "Chloride of Lime" never reaches this figure, the usual percentage of available chlorine being 36-39 per cent Cl. This is because of incomplete chlorination of slaked lime in practice and also because of the decomposition of the calcium hypochlorite formed. The analysis consists of determination of the following:

    (a) Free lime (in "Chloride of Lime")
    (b) NaOH and Na_2CO_3 (in soda bleach)
    (c) Calcium or sodium hypochlorite
    (d) Calcium or sodium chlorate
    (e) Calcium or sodium chloride

For these analyses, take 10 g. sample of "Chloride of Lime" or liquid bleach and suspend it in water, making the volume 1000 cc. in a liter volumetric flask.

(a) **Free Lime.** Pipette 25 cc. of the "Chloride of Lime" suspension made as above and determine free lime as in (a) under XIX.

(b) **NaOH** and **Na$_2$CO$_3$.** Pipette 25 cc. of the liquid bleach solution made as above and determine sodium hydroxide as in (a) and (c) under XVIII.

(c) **Hypochlorite.** Pipette 25 cc. of "Chloride of Lime" suspension or liquid bleach solution into a 250-cc. Erlenmeyer flask and dilute to about 50 cc. Add 15 cc. 10 per cent KI solution and an excess of 0.10N standard sodium arsenite solution (see Note below). Neutralize the solution with dilute HCl, stir constantly for 30 seconds and titrate back with 0.10N I$_2$ solution, using starch as the indicator. This titration takes care of the hypochlorous acid only and is not affected by HClO$_3$. (Note: The standard sodium arsenite solution is made by dissolving 4.95 g. pure sublimed As$_2$O$_3$ in 150 cc. distilled water, to which have been added 15 g. Na$_2$CO$_3$. When solution is complete, add 25 cc. N HCl and make the volume 1000 cc.)

(d) **Chlorate.** Pipette 25 cc. of the "Chloride of Lime" suspension or liquid bleach solution into a 250-cc. Erlenmeyer flask and dilute to about 50 cc. Add an excess of 0.10N standard ferrous sulfate solution and immediately acidify with dilute H$_2$SO$_4$ solution, adding 10 cc. in excess. Cover the flask, shake and titrate excess of ferrous sulfate with 0.10N K$_2$Cr$_2$O$_7$ solution, using 3 drops of 0.01 molar diphenylamine sodium sulfonate solution as the indicator, until one drop of the K$_2$Cr$_2$O$_7$ solution turns the solution reddish violet. This titration gives both the hypochlorite and chlorate. Subtracting (c) from this gives the chlorate.

(e) **Chloride.** Pipette 25 cc. of the "Chloride of Lime" suspension or liquid bleach solution into a 250-cc. beaker and dilute to about 50 cc. Add H$_2$O$_2$ solution to decompose the bleach until the bubbling ceases. Heat just to boiling. Acidify with 6N H$_2$SO$_4$, adding 5 cc. in excess. Add just sufficient ferrous sulfate solution to reduce the remaining hypochlorite and chlorate. Neutralize with dilute ammonia solution, heat to boiling and filter off Fe(OH)$_3$. Cool and dilute the filtrate to about 75 cc. and add 0.2 g. C. P. CaCO$_3$ powder. Titrate with 0.10N AgNO$_3$ solution, using 3 drops of 15 per cent K$_2$CrO$_4$ solution as the indicator in the usual way. This gives total chlorine. Subtracting chlorine from (c) and (d) from this figure gives chloride-chlorine. Calculate to CaCl$_2$ or NaCl as the case may be.

XX. Electrolytic Cell Gases

The gases either from the alkali-chlorine cells or from chlorate cells are to be tested to determine their purity. Oftentimes, this is a very feasible and accurate way of ascertaining the current efficiencies of the cells, *e.g.*, the current efficiencies of a chlorate cell as shown below.

XXA. Cathodic and Anodic Gases from Alkali-Chlorine Cells

The cathodic gas from an alkali-chlorine cell is essentially hydrogen, although there may be a small amount of air. Hydrogen in the gas may be determined by combustion with a known volume of oxygen (air) by

passing the gas over gently-ignited palladium asbestos at a temperature from 300 to 400° C. The gas mixture is passed back and forth three times very slowly so that for the third time the gas is passed, the palladium will hardly glow. Contraction of the volume is caused by the union of hydrogen and oxygen to form water and two-thirds of the contraction in volume represent hydrogen.

The anodic gas is essentially chlorine, but there will always be some CO_2 and perhaps also oxygen. The gas being soluble in water, an Orsat apparatus using mercury or glycerin for displacement is employed. 100 cc. of the gas are usually taken, and chlorine and CO_2 are absorbed in the first pipette containing 25 per cent NaOH solution. Oxygen is next absorbed in the alkaline pyrogallol (sodium pyrogallate) in the second pipette. The balance of the gas may be assumed to be nitrogen.

To determine chlorine, a separate sample of 100 cc. is taken and shaken over 15 cc. saturated KI solution placed on top of mercury in a glass bulb, provided with glass stop cocks. When the cocks are closed and the bulb is shaken chlorine displaces I_2 from KI and the iodine reacts with mercury in the presence of KI so that the red color of liberated iodine gradually disappears. The remaining volume is again measured. The contraction in volume represents chlorine. Deducting this from the Cl_2 and CO_2 determination by the Orsat analysis gives CO_2.

The gas volume is reduced to N.T.P. In all measurements, the barometric pressure must be recorded. Where the gas is not dried, the temperature of the gas in contact with water or with a solution must be observed so that the pressure may be corrected for aqueous tension.

The rate of flow of the gas is measured by means of a gas meter. With the ordinary wet gas meter, the anodic gas must be first scrubbed in NaOH and then washed in water, before it is led through the meter. Thus chlorine and CO_2 are removed and the volume measured is that of oxygen, hydrogen and air.

From the cell gas analysis and the rate of gas generation, it is possible to calculate the cathodic and anodic current efficiencies respectively, when the cell amperage is known. In the alkali-chlorine cells, some chlorine and CO_2 are dissolved in the electrolyte and it is therefore necessary to determine these in the cell effluent. For the determination of dissolved chlorine and CO_2 in the cell effluent, the procedures given under XIX (b) and XVIII (a) and (c) may be followed. When the rate of flow of the cell effluent has been determined, it is possible to find the quantities of chlorine and carbon dioxide so dissolved per hour. From these the cathodic and anodic current losses, and consequently current efficiencies, can be calculated, as will be shown in what follows.

XXB. Mixed Gas from Chlorate Cells

The sum of chlorine and CO_2 in the gases, and then separately chlorine gas alone, are determined as above. The rate of the gas generation is measured by a gas meter after the removal of chlorine and CO_2 by NaOH and washing so that only H_2, O_2 and possibly some air are mea-

sured. Determine O_2 and then H_2 in the gas respectively as in above.

Let $V_s =$ volume of gases after Cl_2 and CO_2 have been scrubbed, in liters per hour at N.T.P.

$p =$ per cent oxygen by volume in V_s as measured.

$p_h =$ per cent H_2 by volume in V_s as measured.

$p_m =$ per cent Cl_2 and CO_2 by volume in the original gases.

$p_c =$ per cent CO_2 by volume in the remaining gas after chlorine has been removed

Call $V_0 =$ volume of original gases reduced to N.T.P. in liters per hour

$f =$ per cent O_2 by volume in the original gases

$f_h =$ per cent H_2 by volume in the original gases.

$f_c =$ per cent CO_2 by volume in the original gases

$f_k =$ per cent Cl_2 by volume in the original gases

$A =$ amperes of current passing through the cell

Then
$$V_0 = \frac{V_s}{100 - p_m} \times 100 \quad \dots \dots \dots (1)$$

$$f = \frac{pV_s}{V_0} = \frac{pV_s}{V_s} \times \frac{100 - p_m}{100} = p\left(\frac{100 - p_m}{100}\right) \dots \dots (2)$$

$$f_h = \frac{p_h V_s}{V_0} = p_h\left(\frac{100 - p_m}{100}\right) \dots \dots (3)$$

$$f_c = p_c \frac{\left(V_s + \frac{f_c V_0}{100}\right)}{V_0} = p_c\left(\frac{V_s}{V_0} + \frac{f_c}{100}\right) = p_c\left(\frac{100 - p_m}{100} + \frac{f_c}{100}\right)$$

Solving for f_c we get:

$$f_c = \frac{100 - p_m}{100 - p_c} \times p_c \quad \dots \dots (4)$$

$$f_k = p_m - f_c = p_m - \left(\frac{100 - p_m}{100 - p_c}\right) p_c \quad \dots \dots (5)$$

From this we get:

$$f_k = \frac{100(p_m - p_c)}{100 - p_c}.$$

Therefore at the cathode,

$$\text{per cent cathodic current efficiency} = \frac{2f_h V_0}{22.4A} \times \frac{96,540}{3600} \times 100$$

$$= \frac{2f_h V_0}{22.4A} \times 26.8 \times 100 = E_1$$

per cent cathodic current loss $= 100 - E_1 = s$

and at the anode,

per cent anodic current loss due to oxygen evolved

$$= \frac{4f V_0}{22.4A} \times 26.8 \times 100 = t$$

per cent anodic current loss due to formation of CO_2

$$= \frac{4f_c V_0}{22.4A} \times 26.8 \times 100 = u$$

per cent anodic current loss due to liberation of chlorine gas

$$= \frac{2f_k V_0}{22.4A} \times 26.8 \times 100 = v$$

Therefore total anode current losses $= t + u + v$

and per cent anodic current efficiency $= 100 - t - u - v = E_2$

Therefore

per cent overall current efficiency of the chlorate cell

$$E = 100 - s - (100 - E_2)$$
$$= 100 - s - t - u - v$$

Alternative Laboratory Methods

Determination of Chlorine in Brine, Ammoniated Brine, Filter Liquor, or other chloride solution using dichlorofluorescein as adsorption indicator.

Pipette 25 cc. of the sample and dilute to 1000 cc. in a volumetric flask. Pipette an aliquot portion of 10 cc. into a 250-cc. Erlenmeyer flask for analysis. Add a drop of phenolphthalein and make the solution slightly acid with dilute nitric acid. Make the volume about 100 cc. Add 6-7 drops of dichlorofluorescein indicator prepared as in Note 1 below, and titrate with $N/10$ silver nitrate solution with constant stirring to coagulate the silver chloride formed until the silver chloride precipitate turns pink and the suspension of AgCl appears just faintly red.

Notes. 1. The indicator is prepared by dissolving 1 g. in 600 cc. of 95 per cent alcohol to which are added 25 cc. $N/10$ NaOH. The volume is then made to 1 liter.

2. This method is accurate even when a very small amount of chloride is present (15-20 mg. Cl. per liter).[*] Its endpoint is sufficiently sharp and with some practice may be readily recognized. Compared with Mohr's method, this method is generally more accurate and gives results with about 0.15 cc. of $N/10$ AgNO₃ less, i.e., Mohr's method takes about 0.15 cc. of $N/10$ AgNO₃ in excess to reach its endpoint. The solution to be titrated should not be more concentrated than 0.01 N in Cl.

3. Unlike Mohr's method, the solution need not be made exactly neutral. A slightly acid solution may be tolerated. This is particularly advantageous when titrating a chloride solution that would hydrolyze to a certain extent.

Volumetric Determination of Sulfate (Hinman's Method)

Preparation of samples. For crude salt weigh 10 g. of sample and dissolve them to make 250 cc. of solution in a volumetric flask. Pipette 25 cc. for analysis. For brine or ammoniated brine or filter liquor, pipette 50 cc. of sample and dilute to 250 cc. in a volumetric flask. Pipette 25 cc. for analysis. For soda ash or crude sodium bicarbonate from filters, weigh 5 g. of sample, and dissolve in 100 cc. of water for analysis.

Preparation of barium chromate reagent. Prepare the barium chromate reagent by precipitating dilute barium chloride solution with potassium chromate solution at the boiling temperature. Filter and wash the precipitate with hot, dilute acetic acid, and then with warm water until free from chromates. Dissolve 3-4 g. of dry $BaCrO_4$ precipitate in 1000 cc. of N HCl in a liter volumetric flask.

Procedure: Dilute the portion taken for analysis to about 100 cc. in a 250-cc. beaker if the volume is not already 100 cc. Make the solution distinctly acid with dilute HCl. Heat to boiling and slowly add a small excess of the barium chromate reagent. Boil for 1 minute (or 5 minutes if any carbonate is present). Digest on a hot plate for 15 minutes. To the hot solution, cautiously add $CaCO_3$ (C. P. powder) in small portions until present in slight excess. (Use ammonia for this neutralization if much iron is present. Then boil off excess ammonia. See Note 3 below.) Cool to room temperature and dilute to 250 cc. in a volumetric flask. Filter through a dry filter paper, rejecting the first 20-30 cc. of filtrate. Then take 100 cc. of the filtrate into a 250-cc. Erlenmeyer flask. Add 2 g. KI and 15 cc. of 12N HCl. Stopper the flask loosely, shake well,

* Kolthoff, I. M., Lauer, W. M., and Sunde, C. J., *J. Am. Chem. Soc.*, **51**, 3273-7 (1929).

and allow to stand for 15 minutes. Titrate slowly with .02N sodium thiosulfate, using the starch indicator in the usual way.

Follow the same procedure, using 100 cc. of distilled water as a blank for correction.

Notes. 1. The principle is based upon the fact that although both barium sulfate and barium chromate are sparingly soluble in cold water, barium chromate is readily soluble in a dilute HCl solution. 1000 cc. of cold water dissolve 2.3 mg. of $BaSO_4$ and 3.8 mg. of $BaCrO_4$, but $BaCrO_4$, unlike $BaSO_4$, may be held in solution by HCl, which displaces $HCrO_4^-$ as it does H_2CO_3, because $HCrO_4^-$ as an acid is comparable to H_2CO_3. If, then, a solution of $BaCrO_4$ in dilute HCl is added in slight excess to a solution containing SO_4^{--} ions, $BaSO_4$ is precipitated but $BaCrO_4$ is not. If the solution is then neutralized, the excess $BaCrO_4$ is also precipitated, leaving an amount of CrO_4^{--} in solution equivalent to the SO_4^{--} originally present. After filtering off the precipitates, CrO_4^{--} in the filtrate can be determined iodimetrically.

2. This method is capable of giving accurate results if the solution taken for analysis does not contain more than 5 mg. of SO_3 per 100 cc. of solution, provided certain conditions as herein mentioned are observed. The result will be high if the barium chromate reagent contains other soluble chromates. Since the solubility of $BaCrO_4$ in hot water is appreciable, the result will also be high if the solution is filtered hot. On the other hand, the result will be low if other chromate is precipitated from the solution with barium sulfate when the solution is neutralized (such as basic ferric chromate). If the solution is not acid enough during the titration of CrO_4^{--} iodimetrically, the reduction of chromate may not be complete, and hence the result is low. Then the return of the blue iodo-starch color within a few seconds after the end point has apparently been reached will be experienced. The reduction of chromic acid by hydroiodic acid is greatly accelerated by high hydrogen ion concentration, thus:

$$CrO_4^{--} + 3HI + 5H^+ \rightarrow Cr^{+++} + 3I + 4H_2O$$
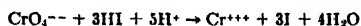
3. When iron, nickel, or zinc is present, the solutions cannot be neutralized with calcium carbonate, because if any of these metallic salts is present, insoluble basic chromate may be formed when the solution is boiled with calcium carbonate. Then too little CrO_4^{--} would remain in the filtrate, causing low results. In such a case, the solution may be neutralized with ammonia, using a small excess, and then the solution is boiled until excess ammonia is expelled, and then filtered.

Alternative methods for the determination of (1) total ammonia, (2) CO_2 and (3) sodium in ammoniated brine, mother liquor, filter liquor and other brine liquors follow:

Preparation of sample. Pipette 10 cc. of the strong liquor into a 250-cc. volumetric flask and make up to the mark. Ten cc. of this dilute solution are pipetted for the following analyses.

Total ammonia. Pipette 10 cc. of the dilute solution into a 250-cc. Erlenmeyer flask. Dilute to 40 cc., add a single drop of 0.1 per cent methyl orange indicator and neutralize with $N/10$ H_2SO_4 solution, adding 10 cc. in excess. Bring the solution in the Erlenmeyer flask to a boil and boil for 15 minutes gently to drive off CO_2. Cool in cold water and neutralize with $N/10$ NaOH. Add to the solution of 15 cc. of 37 per cent formaldehyde solution carefully neutralized with $N/10$ NaOH, using 3 drops of 1 per cent phenolphthalein solution as the indicator. Stir and titrate with $N/10$ NaOH to a red coloration without further addition of phenolphthalein. The number of cc. $N/10$ NaOH in this formaldehyde titration represents total ammonia.

Notes. 1. As the solution contains NH_4Cl it must be made acid with a considerable excess of H_2SO_4 before boiling off CO_2 in order to avoid any possible loss of NH_3 through hydrolysis of NH_4Cl at the boiling temperature. Also, the solution must be made neutral to methyl orange rather than phenolphthalein, in neutralizing back after boiling. If phenolphthalein is used here, the result for total ammonia would be low. In standardizing $N/10$ NaOH with an acid, however, phenolphthalein should be used as indicator.

2. The formaldehyde solution must be first made neutral to phenolphthalein, for methyl orange color is destroyed by formaldehyde. There will be some uncertainty about the end point when neutralizing it with NaOH. The best way is to take out 15 cc. of the 37 per cent solution and dilute to about 50 cc., adding 3 drops of phenolphthalein indicator. Neutralize with $N/10$ NaOH to a faint red coloration. Add this neutralized formaldehyde solution to the solution for titration. The neutralized formaldehyde solution contains enough phenolphthalein so that no more need be added.

3. Care must be taken to boil off CO_2 completely from this strongly acid solution, otherwise the result for total ammonia would be erratic. For this purpose the solution is boiled for 15 minutes in the presence of an excess of H_2SO_4. To avoid any accidental loss during boiling, the Erlenmeyer flask is fitted as follows (Fig. 128).

Carbon dioxide. Pipette 10 cc. of the dilute solution into a 250-cc. Erlenmeyer flask and dilute to 40 cc. Add 30 cc. $N/10$ NaOH, a blank of which must be carried to determine the CO_2 content of the NaOH reagent. Bring the content of the flask to a boil and gently boil off ammonia for 20 minutes using the same arrangement as in the total ammonia determination (see Fig. 128). The volume left after boiling is about 40 cc. Rinse back through the glass tubing with a little water, and while the solution is hot, add 10 cc. of N BaCl$_2$. Immediately stopper the Erlenmeyer, shake, and cool in cold water.
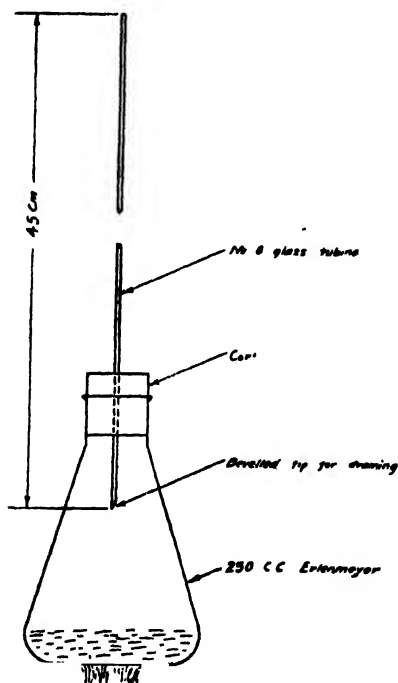
Fig. 128.

Flask for boiling off CO_2 or NH$_3$.

To the cold solution, add 2 drops of phenolphthalein and exactly neutralize with $N/10$ HCl. Then add a drop of methyl orange and titrate with $N/10$ HCl to the permanent end point of methyl orange. The number of cc. of $N/10$ HCl in this methyl orange titration represents CO_2.

Note. With an excess of NaOH, CO_2 will not be lost while ammonia is being boiled off. Any bicarbonate will be converted to carbonate in the presence of NaOH. Precipitation of the carbonate by BaCl$_2$ in a hot solution will not yield a voluminous precipitate of BaCO$_3$ which cannot readily settle. Neutralization to phenolphthalein indicator in the presence of BaCO$_3$ precipitate, must be done in a perfectly cold solution and the endpoint must not be overstepped. The methyl orange titration then gives a sharp end point and the final end point is taken when the red color of the methyl orange will not disappear after 30 seconds of continuous shaking.

Total sodium, Na₂O (Kahane's Method). Pipette 10 cc. of the dilute solution into a 150-cc. beaker. Add 1 drop of 0.1 per cent methyl red indicator and exactly neutralize the solution with N HCl solution, stirring to drive off most of CO_2. The volume will then be about 15 cc. or less. Add to the beaker 100 cc. of the uranyl-magnesium acetate reagent (see Note 3 below), stirring continuously for 5 minutes. Cool in water and lay aside for an hour or more, keeping the temperature at 20° C. The precipitate will be fine, heavy, lemon-yellow crystals. Decant off as much as possible of the supernatant viscous solution without disturbing the precipitate. Add 25 cc. of denatured alcohol (saturated with the uranyl-magnesium-sodium triple acetate), stir and allow to settle again. Decant off this solution similarly taking care not to lose any precipitate. After the second decantation, add about 15 cc. of the denatured alcohol and filter the precipitate through a tared porcelain filtering crucible under suction (as in the Gooch crucible arrangement). Wash out the precipitate from the beaker and wash the precipitate again in the filtering crucible with a little denatured alcohol. Dry the precipitate in the crucible in an electric oven at 108° C. for an hour. The content multiplied by 0.02022 represents Na₂O.

Notes. 1. The presence of ammonia, magnesium and calcium, and also of the carbonates in the ammoniacal brine does not interfere if these directions are followed.

2. The uranyl-magnesium acetate reagent is prepared as follows: Take 32 grams $(UO_2)Ac_2 . 2H_2O$ and 100 grams anhydrous MgAc₂ (or 150 grams MgAc₂ . 4H₂O). Dissolve them in 500 cc. (90 to 95 per cent) denatured alcohol, adding 20 cc. glacial acetic acid and 400 cc. water. Warm to aid solution and make up to 1000 cc. in a liter volumetric flask, when cooled. Let the solution stand overnight. Some precipitate of the uranyl-magnesium-sodium triacetate will have separated out from the sodium carried in the reagents. Filter off the solution into a darkened bottle and keep it in a dark place for use.

The precipitate remaining in the liter volumetric flask is covered with about 500 cc. fresh denatured alcohol. It is shaken and allowed to settle. The alcohol is filtered off and reserved for washing.

3. The supernatant uranyl-magnesium acetate reagent should be decanted off instead of attempting to filter it through the crucible. If it is run through the crucible, the filter becomes so badly clogged that a long time is required for the filtration operation. If these directions are followed, the filtration rate of 50 to 100 drops a minute can be secured, and the whole operation is accomplished in about 15 minutes. This determination for sodium is very accurate even if such a small sample is taken. A portion of this size will give a precipitate weighing about 2.5 grams in the case of strong brine. The method is especially suited when sodium alone in the brine is to be determined.

Oxidation-Reduction Methods Involving the Use of Ceric Ammonium Sulfate *

Many oxidation-reduction reactions may be utilized in determining certain constituents in the chemical analyses conducted in the ammonia soda industry. The iodimetric method is a special type of the oxidation-reduction reaction. The other cases where oxidation-reduction reactions are involved are the volumetric determination of calcium (as calcium oxalate) and of magnesium (as magnesium hydroxyquinolate) in the limestone analysis, the determination of iron in soda ash or in caustic "bottoms," the determination of sodium chlorate in the electrolytic caustic soda, etc. It has been found that ceric ammonium sulfate as an oxidizing agent possesses many advantages, among which may be mentioned its keeping quality (less subject to decomposition on standing), its stability toward elevated temperatures where the reaction must be carried out in hot solution, its high oxidation potential, and its freedom from

* Willard, H. H., and Young, P., *J. Am. Chem. Soc.*, **55**, 3260 (1933).

interference by chlorine in the titration of ferrous iron in a cold chloride solution (in contradistinction to potassium permanganate). However, toward sodium arsenite the reaction is rather slow, and so the addition of a small amount of osmium tetroxide, OsO_4, as a catalyst is recommended. For this purpose, orthophenanthroline-ferrous sulfate is best used as the indicator, giving red coloration in the reducing solution, changing to pale-blue coloration as soon as an excess oxidizing agent is present.

The foregoing reactions are available as alternative laboratory methods and may be illustrated as follows:

In the case of the calcium determination, CaC_2O_4 precipitate is filtered, washed and re-dissolved in a hot dilute H_2SO_4 solution. The solution is heated to about 70° C. and an excess of $0.10N$ ceric ammonium sulfate solution is added with stirring for 30 seconds. A few drops of 0.01 molar OsO_4 solution and a drop of 0.025 molar orthophenanthroline-ferrous indicator are added, and the solution is titrated with $0.10N$ standard arsenious oxide solution until one drop of the arsenious oxide solution turns the solution pink.

In the case of the iron determination, after the reduction of the ferric to ferrous iron by $SnCl_2$ and the addition of $HgCl_2$ and then H_3PO_4 after cooling, the solution may be directly titrated with $0.10N$ ceric ammonium sulfate solution in the cold, using one drop of 0.025 molar orthophenanthroline-ferrous sulfate solution as the indicator, until one drop of the ceric ammonium sulfate solution discharges the pale-pink coloration.

In the case of the $NaClO_3$ determination in the electrolytic caustic soda, to the sample portion is added an excess of standard arsenious oxide solution. Acidify with dilute H_2SO_4, adding a slight excess. Add a few drops of osmium oxide solution as before, then heat to about 55° C. Titrate the excess of arsenious oxide with ceric ammonium sulfate solution, using the orthophenanthroline-ferrous sulfate as the indicator, until one drop of the ceric ammonium sulfate solution discharges the pale-pink color of the solution.

U. S. GOVERNMENT SPECIFICATIONS

Soda Ash

Soda ash shall be of the following types:

> Type I.   58 per cent ordinary or light
> Type II. 58 per cent extra-light
> Type III. 58 per cent dense

Soda ash shall be a high-grade anhydrous sodium carbonate in powdered form and shall be of the type specified by the purchaser.

Soda ash shall conform to the following detail requirements for each type as indicated:

(a) **Chemical Composition.** Soda ash, types I. II and III, after drying for 1 hour at 150 to 155° C. shall conform to the following requirements as to chemical composition:

	Per Cent
Total alkalinity, calculated as Na_2CO_3, maximum	99.2
Sodium bicarbonate ($NaHCO_3$) maximum	.5
Matter insoluble in water, maximum	.25

(b) Loss in Weight at 150 to 155° C. The loss in weight on heating about 2 g., accurately weighed, of the material (types I, II or III) as received for 1 hour at 150° to 155° C. shall not exceed the following limits:

Per Cent

(a) If sample is taken at manufacturer's works, maximum 1
(b) If sample is taken elsewhere, maximum 4

(c) Volume. Thirty grams of the soda ash as received shall have an apparent volume in milliliters for each type indicated, as follows:

	Minimum ml.	Maximum ml.
Type I, light ....:..............	50	65
Type II, extra-light	75	95
Type III, dense	25	35

Methods of Sampling, Inspection and Tests

When packed in cans or cartons—One can or carton shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 50 pounds each. In the case of smaller containers a can or carton shall be taken at random from each lot of containers totaling not to exceed 5000 pounds. The total sample shall in all cases consist of not less than three cans or cartons taken at random from separate containers. With very large lots, where the sample drawn as above will amount to more than 20 pounds, the percentage of packages sampled shall be reduced, so that the amount drawn shall not exceed 20 pounds. Wrap the individual cans or cartons tightly in paraffined paper at once and seal by rubbing the edges with a heated iron. The inspector should accurately weigh each wrapped can or carton, record its weight and the date of weighing on the wrapper, place the wrapped cans or cartons in an air-tight container, which should be nearly filled, seal, mark, and send to the laboratory for test. Samples should be kept cool until tested. The seller shall have the option of being represented at the time of sampling, and when he so requests shall be furnished with a duplicate sample.

When in Bulk. A grab sample of not less than one-half pound shall be taken at random from not less than 1 per cent of the vendor's shipping containers, provided such containers contain not less than 100 pounds each. In case of smaller containers a grab sample of not less than one-half pound shall be taken at random from each lot of containers totaling not to exceed 10,000 pounds. The total sample shall in all cases consist of not less than three grab portions taken at random from separate containers. With very large lots, where the sample drawn as above will amount to more than 20 pounds, the percentage of packages sampled shall be reduced, so that the amount drawn shall not exceed 20 pounds. The inspector should rapidly mix the sample, place in an airtight container, which shall be filled, seal, mark, accurately weigh, record its weight, date of weighing, and place of sampling on the package, and send to the laboratory for test. Samples should be kept cool until tested. The seller shall have the option of being represented at the time of sampling and when he so requests shall be furnished with a duplicate sample.

Preparation of Sample. Rapidly mix the sample; if desired, quarter down to about 1 pound and weigh out all portions for analysis at once. Unused portions of the sample used for analysis shall be preserved in an airtight container in a cool place. Note the condition of the sample. Analyses for carbonate, bicarbonate, and matter insoluble in water shall be referred to the dry basis or carried out on samples previously dried for one hour at 150° to 155° C.

Total Alkalinity as Na_2CO_3. Weigh 5.30 g. of the sample and transfer to a 500-ml. Erlenmeyer flask. Dissolve the sample in about 100 ml. of distilled water, add exactly 100 ml. of 1.0 N H_2SO_4 from a burette, place a small funnel in the neck of the flask, and boil the solution gently for 5 minutes to expel CO_2. Cool, rinse off the funnel and remove it, and then rinse down the sides of the flask. Add 4 drops of methyl red indicator, and titrate back with 0.1 N NaOH. Calculate the total alkalinity as Na_2CO_3, as follows:

$$Na_2CO_3 \text{ per cent} = \text{ml. of } 1.0 \, N \text{ acid} - \text{ml. of } \frac{0.1 \, N \text{ NaOH.}}{10}$$

Sodium Bicarbonate. Weigh 4.20 g. of the sample and transfer to a 250-ml. beaker. Dissolve the sample in about 100 ml. of distilled water at room temperature, and titrate with 0.5 N NaOH until a drop of the solution added to a drop of freshly prepared $AgNO_3$ solution (10 per cent) on a spot plate gives a dark color instantly. Milliliters of 0.5 N NaOH required = percentage of $NaHCO_3$.

Matter Insoluble in Water. Transfer 10 g. of the dried sample to a 400-ml. beaker, add about 200 ml. of freshly boiled distilled water, and boil the solution for 10 minutes. Filter on a weighed Gooch crucible, wash thoroughly with hot water, dry the crucible and residue at 105 to 110° C. for one hour, cool, and weigh. Calculate the percentage of matter insoluble in water.

Loss at 150 to 155° C. Place about 2 g., accurately weighed, of the sample, without previous drying, in a tared wide-mouth short weighing tube provided with a glass stopper. Heat with stopper removed for one hour at a temperature of 150 to 155° C. Insert stopper, cool and weigh. Calculate the loss in weight to percentage.

Volume. Transfer 30 g. of the sample, without previous drying, to a clean, dry 100 ml. graduated glass cylinder, avoiding any packing. Rotate the graduate until the sample flows freely and then, taking care to avoid jarring, level the surface of the sample, and read the volume in milliliters occupied by the sample.

Packaging, Packing, and Marking for Shipment

Packaging. Unless otherwise specified, commercial packages are acceptable under this specification.

Packing. Unless otherwise specified, the subject commodity shall be delivered in standard commercial containers, so constructed as to insure acceptance by common or other carriers, for safe transportation, at the lowest rate, to the point of delivery.

Marking. Unless otherwise specified, shipping containers shall be marked with the name of the material, and the quantity contained therein, as defined by the contract or order under which the shipment is made, the name of the contractor, and the number of the contract or order.

Bases of Purchase

The material should be purchased by net weight, provided the loss in weight at 150 to 155° C. does not exceed 1 per cent. Deliveries based on samples taken at the manufacturer's works and which yield more than 1 per cent loss in weight at 150 to 155° C. should be rejected. Deliveries based on samples taken at any place other than the manufacturer's works and which yield more than 4 per cent loss in weight at 150 to 155° C. should be rejected. With deliveries based on samples taken at any place other than the manufacturer's works and which yield not over 4 per cent loss, settlement should be made on the basis of 1 per cent loss in weight; that is, 0.99 pound of nonvolatile matter should be considered 1 pound of soda ash. For example: Loss in weight at 150 to 155° C. = 3 per cent, then:

$$\text{Net weight of material to be paid for} = \frac{\text{Net weight as received } (100 - 3)}{99}$$

Notes.

This specification covers material suitable for various washing, cleaning and scouring processes, with or without soap, as conditions may require, and where a moderately strong alkaline material is desired.

Soda ash is hygroscopic and it may also absorb some carbon dioxide depending on atmospheric or storage conditions, or both, or on packaging. Therefore, care should be exercised in sampling in order to obtain a representative sample. The inspector should mark the sample to show the place at which it was taken.

This specification is not intended to apply to soda ash used in glass making, but does not preclude the purchase of soda ash suitable for glass making.

It is believed that this specification adequately describes the characteristics necessary to secure the desired material, and that normally no samples will be necessary prior to award to determine compliance with this specification. If, for any particular purpose, samples with bids are necessary, they should be specifically asked for in the invitation for bids, and the particular purpose to be served by the bid samples should be definitely stated, the specification to apply in all other respects.

This specification covers only the types, classes, grades, sizes, etc., of the commodity as generally purchased by the Federal Government, and is not intended to include all of the types, etc., which are commercially available.

Chapter XXIX

Behavior of Soda Ash in Storage

Soda ash, or anhydrous sodium carbonate, is hygroscopic. It absorbs moisture from the atmosphere during storage or transit. A freshly made ash is powdery, loose and free from lumps. It has the tendency to cake or "set" in contact with moisture and consequently becomes lumpy. This often causes a consignment of soda ash to fall below the guaranteed test when the ash has been kept in storage for a long time or shipped a considerable distance. For example, one shipment of soda ash had the analysis given in Table 155.

TABLE 155. Composition of Fresh Soda Ash.

	Per Cent
Na_2CO_3	99.17
$NaHCO_3$	Nil
NaCl	0.71
Water	Nil

After six months in storage it had the composition given in Table 156.

TABLE 156. Composition of Soda Ash After Six Months' Storage.

	Per Cent
Na_2CO_3	82.81
$NaHCO_3$	4.73
NaCl	0.61
Water	11.74

Complaints have frequently come from the customers, stating that the ash has fallen in purity and that a considerable amount of water has been found in the product. If the ash is sold to the block makers, very likely they will find that it will not "set" to a hard block with the normal amount of water employed. On close examination it is found that the weight per bag or per barrel has increased correspondingly, so that while the alkali content has decreased, the bulk weight has increased. No loss in soda has really taken place. The sample showing considerable water and bicarbonate gave, on calcination in the laboratory until free from water and bicarbonate, the same test as when it left the works.

Moreover, samples from different parts of the same bag may yield quite different results. One dense ash consignment consisting of 200-lb. bags of dense ash each gave two analyses shown in Tables Nos. 156 and 157.

From the tables it will be seen that the outer portion of the bag has absorbed more moisture and more CO_2 from the air than the inner portion. The density of the outer portion is also higher. Hence sampling is a very important factor.

TABLE 157. Analysis of a Dense Ash Sample Taken from
Outside Portion of a Bag.

	Per Cent
Na_2CO_3	89.26
$NaHCO_3$	2.84
$NaCl$	0.50
Na_2SO_4	0.15
Fe_2O_3	0.001
Insoluble matter	0.04
Water	7.19
Ca^{++}	nil
Mg^{++}	nil
Density (by loosely-packed method)	0.998

TABLE 158. Analysis of a Dense Ash Sample Taken from
Center of the Same Bag.

	Per Cent
Na_2CO_3	92.00
$NaHCO_3$	1.99
$NaCl$	0.53
Na_2SO_4	0.15
Insoluble matter	0.04
Fe_2O_3	0.001
Water	5.29
Ca^{++}	nil
Mg^{++}	nil
Density (by loosely-packed method)	0.987

The amount of water and carbon dioxide that the ash will absorb depends upon the climatic conditions (*i.e.*, the humidity and the temperature of the air), the extent of exposure to the atmosphere and the length of time. Light ash is more readily affected by atmospheric moisture and CO_2 than dense ash. A kind of light ash that had been kept for 9 years (from 1921-1930) in a stoppered bottle gave the composition shown in Table 159.

TABLE 159. Composition of Light Ash After Nine Years' Storage.

Analytical Results	Per Cent	Calculated Results	Per Cent
Insoluble matter	0.03	Insoluble matter	0.03
Na_2CO_3	51.25	$Na_2CO_3 . H_2O$	16.23
$NaHCO_3$	29.62	$Na_2CO_3 . NaHCO_3 . 2H_2O$	79.69
$NaCl$	0.95	$NaCl$	0.95
Fe_2O_3	0.002	Fe_2O_3	0.002
Water	18.11	Free moisture	3.06

and a sample of granular dense ash kept for the same length of time and under the same conditions gave the results shown in Table 160.

TABLE 160. Composition of Dense Ash After Nine Years' Storage.

Analytical Results	Per Cent	Calculated Results	Per Cent
Insoluble matter	0.05	Insoluble matter	0.05
Na_2CO_3	72.62	$Na_2CO_3 . H_2O$	68.81
$NaHCO_3$	10.94	$Na_2CO_3 . NaHCO_3 . 2H_2O$	29.43
$NaCl$	0.88	$NaCl$	0.88
Fe_2O_3	0.003	Fe_2O_3	0.003
Water	15.44	Free moisture	0.76

TABLE 161. The Change Which Soda Ash Undergoes During Storage.
(Per Cent by Weight.)

Duration in Days	Analyzed Results				Calculated Results				Absorption of		Ratio of Water to CO_2	Difference Between Water and CO_2	Water in	
	NaCl	Na_2CO_3	$NaHCO_3$	Water	NaCl	Na_2CO_3	Na_2CO_3 .H_2O	Na_2CO_3 $NaHCO_3$.$2H_2O$	CO_2	Water			Na_2CO_3 .H_2O	Na_2CO_3 $NaHCO_3$.$2H_2O$
0	1.91	97.90	Nil	0.03	1.91	97.72	0.21	Nil	Nil	Nil	....	Nil	0.03	Nil
15	1.84	94.10	1.65	1.98	1.84	84.54	8.75	4.44	0.43	2.16	5.02	1.73	1.27	0.71
28	1.90	88.05	2.85	7.25	1.90	48.93	41.55	7.67	0.75	7.55	10.1	6.80	6.03	1.22
43	1.89	85.33	3.36	9.22	1.89	35.27	53.60	9.04	0.88	9.58	10.9	8.70	7.78	1.44
57	1.91	85.45	3.36	9.32	1.91	34.80	54.29	9.04	0.88	9.68	11.0	8.80	7.88	1.44
71	1.62	83.34	5.03	10.08	1.62	30.45	54.57	13.53	1.32	10.62	8.04	9.30	7.92	2.16
85	1.66	83.24	5.05	10.06	1.66	30.34	54.43	13.58	1.32	10.60	8.03	9.28	7.90	2.16
99	1.84	82.96	5.71	9.48	1.84	34.35	48.43	15.26	1.50	10.09	6.73	8.59	7.03	2.45
113	1.78	81.13	7.28	9.87	1.78	30.28	46.51	21.49	1.91	10.65	5.58	8.74	6.75	2.12
127	1.51	79.60	8.48	10.50	1.51	28.44	47.33	22.81	2.22	11.41	5.14	9.20	6.87	3.63
141	1.58	77.83	10.03	10.55	1.58	28.36	43.06	26.99	2.63	11.62	4.42	8.99	6.25	4.30
155	1.75	78.23	9.62	10.50	1.75	28.51	43.96	25.88	2.52	11.53	4.58	9.01	6.38	4.12
169	1.73	76.88	11.00	10.39	1.73	29.63	39.14	29.50	2.88	11.57	4.02	8.69	5.68	4.71
183	1.63	75.26	12.89	10.22	1.63	31.31	32.38	34.68	3.37	11.60	3.44	8.23	4.70	5.52
197	1.70	74.93	12.47	10.90	1.70	26.45	38.31	33.54	3.27	12.23	3.74	8.96	5.56	5.34
211	1.76	74.37	13.26	10.61	1.76	29.60	33.97	35.67	3.47	12.03	3.47	8.56	4.93	5.68
225	1.63	73.40	13.69	11.30	1.63	23.44	38.10	36.85	3.59	12.76	3.55	9.17	5.53	5.77
239	1.72	73.28	14.02	10.98	1.72	26.26	34.31	37.71	3.67	12.48	3.39	8.79	4.98	6.00
252	1.53	71.21	15.79	11.50	1.53	23.40	32.59	42.51	4.14	13.19	3.19	9.05	4.73	6.77
266	1.54	69.53	16.96	11.97	1.54	20.45	32.38	45.63	4.44	13.78	3.10	9.34	4.70	7.27
280	1.58	69.94	17.04	11.39	1.58	24.34	28.18	45.85	4.46	13.21	2.96	8.75	4.09	7.30
293	1.48	69.43	16.67	12.48	1.48	16.94	36.79	44.85	4.57	14.26	3.26	9.89	5.34	7.14
307	1.47	68.52	17.87	12.04	1.47	19.83	30.52	48.08	4.68	13.95	2.98	9.27	4.43	7.61
322	1.42	67.83	18.62	12.18	1.42	19.59	28.94	50.10	4.87	14.17	2.91	9.30	4.20	7.98
337	1.45	68.17	18.46	11.94	1.45	21.23	27.67	49.66	4.84	13.92	2.88	9.08	4.03	7.91
351	1.81	67.48	18.83	11.89	1.81	21.22	26.32	50.66	4.93	13.90	2.82	8.97	3.82	8.07
365	1.82	66.86	19.22	12.43	1.82	17.93	28.87	51.71	5.04	14.49	2.87	9.45	4.19	8.24

For many purposes, the presence of moisture and bicarbonate in the ash is not objectionable, but for certain purposes, such as for soda block making, it may cause the ash to lose much of its "setting" property.

The change which soda ash undergoes in contact with the atmosphere has been the subject of some study. It not only reveals the nature of the change the ash undergoes on exposure to the atmosphere, but it also throws much light on the formation and composition of natural soda deposits. A bag of freshly made soda ash is sent to the laboratory and kept in a dry place. A sample is taken from it once every two weeks and the necessary analyses made thereon. In this way the change in the ash is observed by means of a bi-weekly record during a period of a whole year. The results are given in Table 161.

The results in Table 161 show that in the course of 365 days soda ash has picked up more than 14 per cent of water but only 5 per cent of CO_2. It absorbs moisture from the air more readily than it does CO_2, and takes up moisture very rapidly in the beginning before it takes any material amount of CO_2. Moisture seems to have been taken in to form first the monohydrate ($Na_2CO_3 . H_2O$) which then in turn is gradually transformed into the sesquicarbonate with the absorption of CO_2 and a further amount of moisture. This is shown by the fact that the monohydrate, which is formed in comparatively large quantities at the begin-
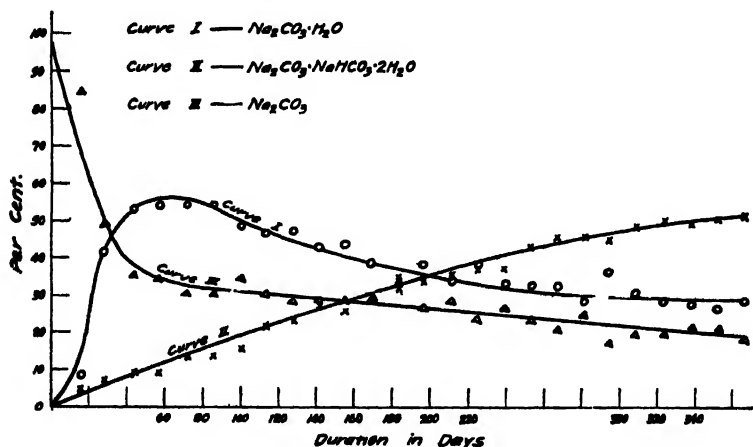
FIG. 129. Curves showing percentages of $Na_2CO_3 . H_2O$, $Na_2CO_3 . NaHCO_3 . 2H_2O$, and Na_2CO_3.

ning, rises rapidly to a maximum; then it decreases and at the same time the quantity of the sesquicarbonate formed steadily increases (see Curves I and II, Fig. 129). Had we continued to keep record of the change for a number of years it would have been found that all the soda ash (anhydrous carbonate) would have disappeared and that all the monohydrate would have been converted in time to the sesquicarbonate form. In other words, all the soda ash would eventually be changed to the sesquicarbo-

nate as the final stable form in contact with the atmosphere. The difference between the amount of water absorbed and that of CO_2 absorbed also points in this direction, as the value has increased to over 9 per cent and was slowly increasing, approaching the value of 10.17 per cent, which is the theoretical difference in the percentages of water and CO_2 in the
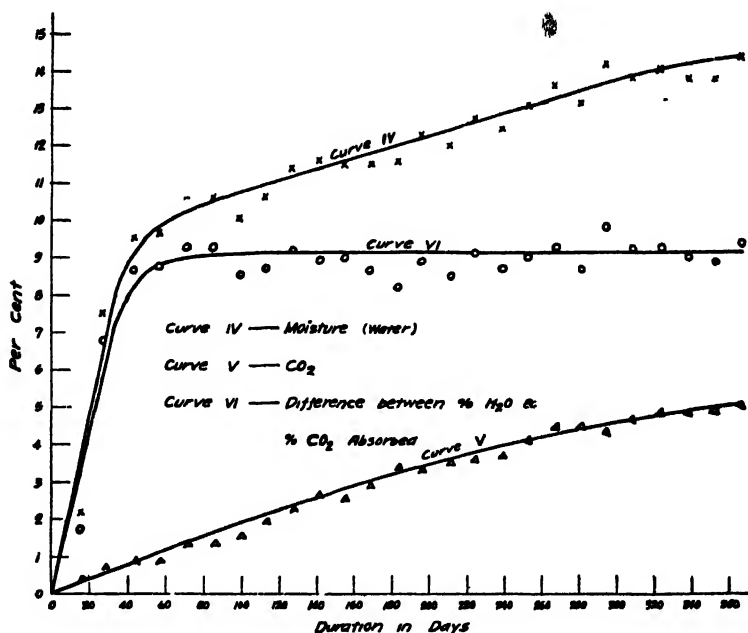
FIG. 130   Curves showing absorption of moisture and carbon dioxide by soda ash on exposure to the atmosphere during storage.

pure sesquicarbonate from the pure anhydrous sodium carbonate (Curves IV and V, Fig. 130).   Thus,

$$3Na_2CO_3 + 5H_2O + CO_2 \rightarrow 2[Na_2CO_3 . NaHCO_3 . 2H_2O]$$
$$318 \qquad\quad 90 \qquad 44 \qquad\qquad\qquad 452$$

$$\left(\frac{90}{452} - \frac{44}{452}\right) \times 100 = 10.17\% = \text{Difference between } \% \text{ } H_2O \text{ and}$$
$$\% \text{ } CO_2 \text{ absorbed in the sodium sesquicarbonate}$$
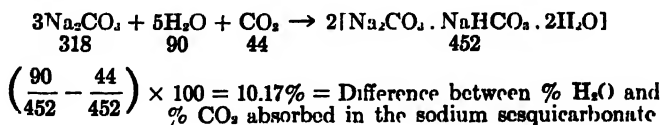
Again, the ratio of water absorbed to that of CO_2 first increases to a maximum of 11, then decreases to less than 3; and the trend of the curve shows that it would continue to decrease approaching the theoretical value of 2.04, which is the theoretical ratio of water to CO_2 absorbed by pure anhydrous sodium carbonate to form pure sesquicarbonate as the ultimate product.

In spite of the continued increase in the water absorbed in the soda ash, the percentage of $Na_2CO_3 . H_2O$ steadily decreases (see Curve I, Fig. 129), showing that $Na_2CO_3 . H_2O$ is going over to the $Na_2CO_3 .$ $NaHCO_3 . 2H_2O$ form faster than is formed from the soda ash. It is not

unlikely that at the end there will come a time when all the $Na_2CO_3 . H_2O$ will have disappeared and the exposed mass then will consist of all $Na_2CO_3 . NaHCO_3 . 2H_2O$ if the process is allowed to proceed indefinitely. But as the course of the change was followed for only 365 days, it is difficult to judge from the curves obtained when that time may come, *i.e.*, how long it will take to reach that condition, starting with anhydrous soda ash, because the curve flattens out, asymptotically approaching the theoretical value. Nevertheless, it gives us a good hint as to the manner of formation of the natural trona or urao, and a theory as to why the sesquicarbonate is the most favored form of deposit in nature, although the sesquicarbonate with the formula $Na_2CO_3 . NaHCO_3 . 2H_2O$ represents an ideal composition which all natron deposits only more or less closely approach in composition.
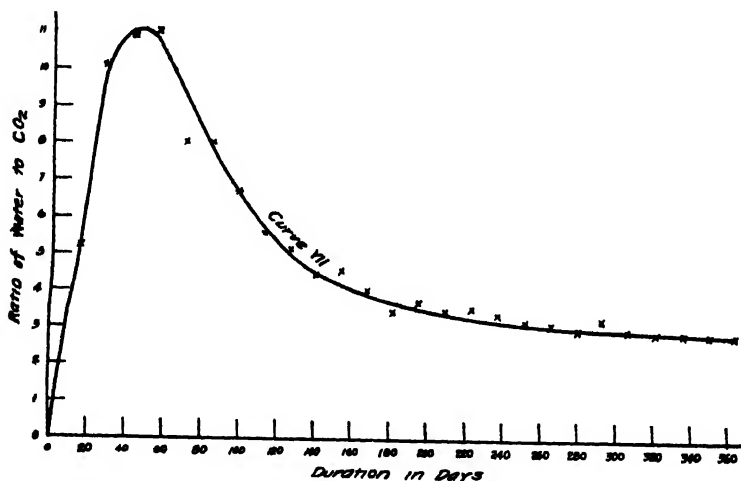
Fig. 131. Curve showing ratio of water to carbon dioxide absorbed by soda ash.

The manner of formation of trona or urao in the earth crust is explained thus: Water carrying soda in solution is collected in a depressed region and is concentrated by natural evaporation due to the dryness of the climate, the scarcity of rain, and the presence of more or less constant winds in these open places. Concentration of soda in the water becomes so great that during cold weather sal soda begins to crystallize out on the surface of the marshy ground. The upper layer of the sal soda deposit gradually effloresces in contact with the atmosphere and loses much of its water of crystallization, forming the white powdery monohydrate $Na_2CO_3 . H_2O$. This in turn is gradually converted by atmospheric H_2O and CO_2 to the sesquicarbonate as the ultimate stable form. We have thus:

$$Na_2CO_3 \text{ (diss.)} \rightarrow Na_2CO_3 . 10H_2O \text{ (cryst.)} \rightarrow$$
$$Na_2CO_4 . H_2O \text{ (powder)} \rightarrow Na_2CO_3 . NaHCO_3 . 2H_2O$$
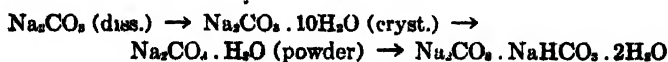
Coming back to the question of the weathered soda ash during storage or transit, how are we to distinguish it from an underfinished or wet ash? That is, how are we to determine, upon receipt of a sample of soda ash containing moisture and $NaHCO_3$, whether it was a good ash but merely weathered by long storage, or whether it was originally a kind of under-finished soda ash as it left the dryers? A weathered ash had, as we saw above, a high percentage of water with a comparatively low percentage of CO_2 and the percentage of total water absorbed in the ash is always greater than twice that of CO_2, approaching 2.04 as the theoretical limit for pure sodium sesquicarbonate (see Curve VII, Fig. 131). An under-finished ash contains far less moisture in proportion to the excess of CO_2 in the form of $NaHCO_3$. In calcining crude filter bicarbonate, the last traces of ammonia and water are driven off far more readily than the remaining portion of $NaHCO_3$, and an underfinished ash may contain as much as 3 to 5 per cent $NaHCO_3$ and yet a very small fraction of one per cent of water. Consequently, from the proportion of water and excess CO_2 in the ash, it is not difficult to differentiate a weathered ash from an underfinished ash, but when an underfinished ash has further been excessively weathered, there is no way to tell whether or not this weathered ash was originally a well-finished ash. Its past history then cannot be determined. Table 162 gives the composition of a sample of underfinished ash.

TABLE 162   Composition of Underfinished Soda Ash

	Per Cent
Insoluble matter	0 06
Na_2CO_3	79.55
$NaHCO_1$	16 80
NaCl	1 54
Fe_2O_3	0.005
Water	1.89

With the $NaHCO_3$ as high as 16.8 per cent, the amount of water present is only 1.89 per cent. If this were a weathered ash, to correspond to this high percentage of $NaHCO_3$, the water absorbed would be considerably more than 10 per cent.

Chapter XXX

Layout, Design and Location of Ammonia Soda Plant

Ammonia soda plants require as raw materials the following commodities arranged in the order of quantities required:

(1) Salt (rock salt brine or sea brine)
(2) Limestone
(3) Coal
(4) Coke
(5) Ammonia [crude liquor or $(NH_4)_2SO_4$]
(6) Sulfide of soda, or 60 per cent Na_2S [when $(NH_4)_2SO_4$ alone is used]

Arranged in the order of the expenses involved per ton of soda ash made (quantity and cost) these raw materials stand as follows:

(1) Coal
(2) Limestone
(3) Salt

(4) Coke
(5) Ammonia
(6) Sulfide of soda

The latter arrangement may vary somewhat for different plants because the comparative costs of coal, salt, and limestone entering the manufacture depend upon the relative location of the plants in regard to the sources of supply of these materials, their quality, and their prevailing prices in a particular locality.

The prices of the first three raw materials when they are plentiful and their source is in close proximity to the works may be as low as:

Salt in the form of brine $0.50 per ton, delivered at plant
Limestone $0.60-$0.75 per ton, delivered at plant
Coal $2.00-$3.00 per ton, delivered at plant

But it is seldom that a site for an ammonia soda plant can be so fortunately located as to have all three raw materials in close proximity, at the minimum prices, and in large quantities. With soda ash at its normal price, plants obtaining these raw materials at prices varying from 100 to 300 per cent higher than the above figures operate at a good profit, especially when they have a moderately large output.

The foregoing is a direct cost dealing with cost of raw materials only. In the following we shall include also the indirect costs, thus approaching more nearly the cost statistics of a plant operation. These may be arranged as follows:

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(1) Fuel
(2) Labor
(3) Limestone
(4) Salt

(5) Ammonia
(6) Some form of sulfur
(7) Factory supplies

The positions of the first two items might be reversed in locations where fuel is exceptionally cheap and where the proper arrangement of equipment for reasonably low attendance labor does not exist.

In only the most exceptional circumstances could limestone be more expensive than either of the first two items, although occasionally salt may cost more than limestone. The last three items are frequently in other relationships to one another since they depend on many factors. They have been included because they have some bearing on the selection of the plant site, and their effect will be discussed briefly in this chapter. "Depreciation and obsolescence" at the customary rate of 10 per cent on, say, a $15,000 investment per ton of daily capacity in soda ash and a 70 per cent annual load factor introduce a cost per ton which leads the above list by an appreciable margin. It is thus obvious that the lowest possible initial cost of plant is important to low-cost production. A layout which results in low initial cost and yet permits the above seven items to have a low total is obtained only from capable, highly experienced design engineers. This chapter does not attempt to describe all the factors and variables entering into the problem of obtaining the best layout and design of an ammonia soda plant; it merely calls attention to the effects of some of the more important variables.

Favorable unit prices for the four large items given in the foregoing list follow. These are delivered prices and represent a fairly plentiful supply close to the sites under consideration. Occasionally some one of the materials may be even higher. Well designed plants can be operated at a profit where raw material prices are considerably higher, since then the soda price is generally also higher.

(1) Fuel
    (a) Coal, $3 per ton, or 11 cents per million Btu.
    (b) Coke, $6.50 per ton, or 23 cents per million Btu.
    (c) Bunker "C" fuel oil, $0.85 per barrel or 13.5 cents per million Btu.
    (d) Natural gas, 15 cents per thousand cubic feet or 15 cents per million Btu.

(2) Attendance and Maintenance Labor (weighted mean of all classes needed)
    $0.65 per man-hour

(3) Limestone
    $0.60-$0.75 per ton stone, as already given

(4) Salt, as saturated raw brine
    $0.50 per ton NaCl, as already given

There is almost nowhere a peculiarly favorable site where all the raw materials and intelligent labor required at the lowest unit prices can be found. Furthermore, it is the alkali manufacturer's problem to deliver his product to his customer's doorstep at the least possible cost. In selecting a site he must therefore consider not only the purchase and transportation of raw materials to his plant, but also the transportation of his soda products to the plants of his customers (or potential customers).

The layout of an ammonia soda plant is a matter largely of local conditions and individual preference. However, there are some general rules on which those qualified to make a design will agree. For instance, the boiler room should be located adjacent to the engine room furnishing steam to the carbon dioxide compressors, electric generators, exhausters, cooling water pumps, air compressors and other steam-driven machinery; and the lime department should be adjacent to the distiller house so that the concentrated milk of lime can be sent to the distillers in short pipe lines. Next to the distiller house should come the ammonia absorber house, with an adjoining space for the location of settling vats. Next comes the tower house taking the ammoniated brine from the vats in the absorber system. The furnace room is located reasonably near the tower house so that crude bicarbonate can be taken from under the filters in belt conveyors to the furnaces and the returned gas from the furnaces sent back to the columns through a set of condensers. The engine room, where all the steam-driven machinery, the carbon dioxide compressors, etc., are located, should be sufficiently close to both the furnace room and the tower house to bring the gas from the furnaces through scrubbers and coolers to the columns and at the same time take the kiln gas from the lime kilns through a kiln gas scrubber. The carbon dioxide compressors, the generators, the exhausters, the cooling water pumps and the air compressors may be advantageously steam driven, and the exhaust steam utilized for the distillation of ammonia in the distiller house. Outside of the engine room in the various houses, the machinery is individually driven by electric motors.

The buildings in an ammonia soda works are usually high. The distiller house must be high enough to accommodate the tall distillers together with the condensers. It is general practice to put the heater on top of the lime still, and the condensers on top of the heater, making the overall height of the whole apparatus over 100 feet. The distiller house is then at least 125 feet high and frequently much higher.

In the absorber house, the elevation of the bottom of the absorber must be above the top of the settling vats, so that the ammoniated brine can flow to the vats by gravity. The vats are located on the main floor on pedestals high enough to provide a working height to pump "mud" from the bottom. On the top of the absorber can be located an ammonia gas cooler, and on top of this the absorber washer, necessitating a height about 80 feet for the absorber house. In between the bottom compartments of the absorber and the middle passette, the partially ammoniated

brine is cooled in outside surface coolers (absorber coolers) before final ammoniation at the absorber bottom.

In the tower house are located the columns, or carbonating towers, from 75 to 80 feet high. The exit gas containing ammonia passes through a cyclone separator located near the top of the tower and is scrubbed in washers called tower washers, whose bottoms are below the top of the towers, but must be above the inlet point in the inlet compartment of the absorber washer to avoid the use of a centrifugal pump. The brine from the bottom of the tower washers, containing some ammonia, flows to the middle compartment of the absorber washer through a long U-loop seal. The brine from the bottom of the filter washer enters the tower washer at a few sections below the top compartment. The filter gas washer must be located on a higher level (not less than 10 feet above the top of the tower washer) so that the brine from the bottom of the filter washer can flow by gravity with a U-loop seal to the inlet compartment in the absorber washer from a higher vacuum on the filter washer side, or to the inlet compartment at the tower washers against pressure on the tower washer side. This arrangement avoids the necessity of having centrifugal booster pumps to send brine from the bottom of the filter washer to the inlet compartment of the absorber washer or of the tower washer. The total height of the tower house including the washer house portion is over 120 feet. On top of the roof may be situated a large brine storage tank feeding fresh brine by gravity to the top of the tower washers, the filter washers and the absorber washers. The draw liquor being cold, very little brine is required to scrub ammonia from the gas in the filter washer. The absorber washer and the tower washer are the two places where fresh brine is required in proper quantities. The bicarbonate filters are generally located on a floor at least 30 feet above ground so that the filter liquor can flow down to the filter liquor main under high vacuum with sufficient liquor leg for a seal. From the filter trap, or separator, the gas is piped up to the bottom of the filter washer, located on an approximately 100-foot level.

In the lime department, the lime drawn from the bottom of the kiln may be elevated to a bin in bucket elevators. From the bin the lime is fed to a rotary slaker by means of a conveyor feeder. The discharge end of this horizontal slaker must be high enough to allow the rejected "sand" to be hauled out in cars from the main floor and the milk of lime to flow by gravity to a lime well (or storage tank) situated on the main floor, where the lime pump sends the milk of lime to the distiller. With the lime kiln standing above the building, the total height of the house should be about 50 feet. On top of the lime kiln, there should be a working platform to which access may be gained conveniently by means of a stairway or elevator.

The furnace room contains the rotary furnaces and the conveyor system, with a clear floor space on the top for storing and feeding bicarbonate to the furnaces below. The building need not be over 45 feet high. It is one of the lowest buildings in the whole plant. The soda conveyors

can go outside of the building or between buildings. A good overhead space, however, must be provided so that the place may not be too hot or oppressive to the workmen. Ventilation points should be freely provided in the roof construction; otherwise the hot atmosphere in a low room coupled with the soda dust and ammonia gases (to a certain extent unavoidable) may make the place quite uncomfortable to the workmen. This applies to the space required over the conveyors as well as over the dryers.

The boiler room is normally just high enough to accommodate the boilers and their accessories and its height depends upon the type of boilers installed, but a full-height basement must be provided for hauling out the ash. The engine room is a low building, generally one story high, to house various machinery; but it must be high enough to allow an overhead space under the trusses for installing a travelling crane. It must also have a full-height basement to house various steam lines, exhaust lines, etc.

The packing room and the rest of the buildings are low and generally not more than two stories high, but high enough to house various soda ash elevators and conveyors. But the main or ground floor of all the houses in the works should be located 10-12 feet from the normal ground level with a full-height basement on the ground level. This basement space may be utilized for ash hauling (in the boiler room), for locating steam mains and exhaust mains (in the engine room), and for locating various gas liquor and water pipes and also waste liquor sumps (in the tower and distiller houses). This arrangement sets the working floor at 10-12 feet above ground level with various pipes introduced below the floor and yet allowing a clear space overhead for working in the basement. It is both a neat and convenient arrangement.

The packing and loading facilities for the dry products should be immediately adjacent to loading tracks and docks. There should also be proper approaches for motor trucks. The docks for handling products onto both trucks and railroad cars should be designed for minimum labor. The raw material storage yard and the finished product storage should be located near the shipping points, in order to facilitate moving the raw materials in and sending the finished products out.

The packing and shipping buildings should be reasonably close to the rotary furnace building so that conveyors for the dry products may be as short as possible. This minimizes power consumption, maintenance cost and breakdown hazards. Prior to the filter operation, substantially all the materials are in the liquid state so that the arrangement of buildings need sacrifice relatively little of the requirements of short pipe lines. Pipe lines are very cheap compared to dry product conveyors. From the filters on, the handling of the solids by conveyors starts. The furnace room needs to be within good conveying distance of the crude bicarbonate filters.

There must be a storage reservoir for cooling water and another for brines. If these reservoirs can be placed as high as needed to feed into

all apparatus by gravity, an advantage is gained in that no pump is required and the hazard of pump breakdown is thereby eliminated.

The buildings are of either steel or reinforced concrete structure (preferably the former), and must be heavy to take care of the heavy, tall, cast-iron apparatus. The foundation must be made of heavy reinforced concrete (made waterproof) with concrete or timber piles driven under each piece of heavy apparatus, such as the ammonia distillers, the carbonating towers, etc., where the whole load is concentrated on a small base. Overhead inter-building pipes should be supported from the trusses or beams, while those underground pipes between buildings should be located in a tunnel or trench, but not buried in the soil, so that settling of the buildings at either end will not throw strain on the pipes, and also so that repairs may be made conveniently. Where a pipe passes through a brick wall, clearance above the pipe in the wall should be allowed so that settling of the wall will not bear on the pipe. This applies especially to cast-iron pipes, which are used extensively in the works. Sewers and fire hydrant lines should be located below ground around the buildings. Cooling water from the exit of different units of the apparatus is run off to the sewers, but the distiller waste liquor must be sent out with or without a booster pump to an open field for settling or to a large body of water through pipes or in a specially constructed channel or canal.

The materials used in the construction of buildings and equipment depend to some extent upon local supplies. As pointed out in earlier chapters, the apparatus for handling ammoniated brine and filter liquor must be of cast iron; high-copper alloys are entirely unsuitable. Building frames constructed of mild steel will suffer from corrosion, and factors of safety in the original design must take this into account Timber buildings are reasonably resistant, but are exposed to fire hazards. Concrete made of ordinary silica sand and a coarse aggregate of good rock does reasonably well for floors if they are amply pitched to minimize the effect of puddles of corrosive liquor.

In the caustic plant, concrete floors should be very steeply pitched and the design must be carefully prepared to avoid seepage of caustic liquor under important weightbearing footings. Although concrete is not very resistant to caustic there is no other suitable material having an economical advantage over the usual local concrete. The dust in the air near the caustic operations is corrosive enough to deserve careful consideration in the design.

The tallest buildings in an alkali plant afford protection to portions of apparatus which rarely have men near them. It is sometimes advisable to consider the climate and the cost of a simpler type of protection, such as heat insulation, painting, weatherproofing, etc. of the apparatus and piping rather than a housing over them.

The following summary gives a broad consideration regarding general requirements in the layout and the design of an ammonia soda plant:

(1) It must fit the contours of the land and take best advantages of high and low points.

(2) It must bear a proper relationship to existing or potential railroads, motor highways, docks and waterfront.

(3) It must be arranged for lowest handling costs.

(4) It must be arranged to permit extension of the plant and leave room for additional units or for possible by-product operations.

(5) Interconnecting piping and material conveyors should be as short as possible.

(6) Apparatus should be arranged so that direct attendance labor can control a maximum of the operations.

(7) It should leave room for adequate storage of raw materials and finished products.

(8) It should bring about minimum maintenance cost.

Since the contours of the actual site and the variations in the elevation of the ground affect the building arrangement more than any other factor, no hard and fast rule can be laid down for the best arrangement. A number of expedients are possible for reducing installation costs by compact, and yet not cramped, layout. Further improvement can be attained by ingenious interrelation of equipment so that a single operator can adequately attend a maximum of it. Not only does this save money in direct operating labor cost, but a more adequate control is possible where a single individual depends least on the cooperation of others. Unfortunately, no direct statement as to how this is achieved can be made because, depending on the best location for railroad and docks, the various products to be manufactured, etc., certain operations will be adjacent to each other in one plant and not in another.

SELECTION OF PLANT SITE

For the location of an ammonia soda plant the site must fulfill the following main requirements:

(1) General Requirements
a) Good transportation facilities preferably both by boat and by rail.
(b) Sufficient nearness to the market or to the center of distribution.

(2) Particular Requirements
(c) Close proximity to the sources of salt, limestone, and coal (and consequently also coke and crude liquor).
(d) Plenty of underground cold water available for cooling.
(e) Ample land or waterway available for waste disposal.

If all these requirements cannot be met, expert judgment is necessary to decide, by a detailed study of the conditions, which of the above items are most essential. For example, if both salt and limestone are not

available close together, it may be better to locate the plant near the source of supply of limestone and transport the salt, than vice versa, since salt can be transported in the form of brine at little cost.

Items (a) and (b) above apply to most industries and are therefore the general requirements for any given industry. They will not be discussed in detail here, as this is quite evident.

As salt (in the form of rock salt brine or sea brine), limestone, and coal are the three main raw materials in soda ash manufacture, it is necessary that these materials be plentiful and cheap, and their continuous supply assured. The first two, salt and limestone, furthermore, must be produced by the manufacturers of soda ash. The soda works must own and operate salt wells (in the case of rock salt brine) or salt fields (in the case of sea brine), and quarry their own stone. As these are the two raw materials used in the largest quantities, the economical development of the works depends upon a cheap and inexhaustible supply of both. They must also be of good quality, especially the limestone. A poorer grade of limestone is very uneconomical to use. Coal can be purchased on the open market but it must be sufficiently cheap. Where bituminous coal is abundant, and coal mines are not far away, crude ammonia liquor and coke will be available from the gas works. Coke is a standard commodity that can be bought in the market, but the crude liquor must be secured from the gas works by special arrangement. Ammonia and coke, though used in comparatively small quantities, constitute important materials in the ammonia soda process because of their comparatively high cost, so much so that the manufacturers frequently operate their own by-product coke ovens. The crude liquor is desirable not only because it is a cheap source of ammonia but also it contains the sulfide required for the system. At present some synthetic ammonia is being used, and sodium sulfide is all the more necessary in the process. All these enter into the consideration of a plant site.

The question of water supply is important. Not only is water used in large quantities in the boilers for power generation, but a much larger quantity is needed for various cooling purposes. The requirements for the two purposes may not be the same. The surface water, e.g., river water, while it may be very good for the boilers, is not suitable for cooling, as the temperature may be too high in summer. On the other hand, well water may be too hard for boilers but it is excellent for cooling purposes. A good source of supply of cooling water is from artesian wells, as it is practically at a constant temperature (16 to 18.5° C. in summer and winter at 400 to 500 feet below the surface level). Good water is comparatively difficult to obtain for plants which are located near the sea-coast, where sea brine may be used as the source of the salt supply and where probably only well water will be available for the boilers. For small works, the quantity of cooling water required is in the neighborhood of 2,000 to 2,500 cubic feet per ton of ash. For large works it is less per ton of the output; but much depends upon the cooling

surface available, the design of the apparatus, and the arrangement of different cooling units. Therefore cooling water is a factor in the choice of the site.

The distiller waste is always a source of trouble. The quantity is large (about 350 cubic feet of liquor per ton of ash) and its disposal in public waterways has been in most cases prohibited by law. Calcium chloride in solution permeates the ground and finds its way to the underground water. It causes excessive chlorine in the soil. Solids separating out from the waste do not readily become hard and firm. If the waste liquor is sent directly into a river, its lime and calcium chloride content may be objectionable. Besides, the solids carried in it may silt up the river. Its satisfactory disposal has become a problem unless the works is fortunate enough to be located near the sea, near a big lake, or among the hills (in this last place, the waste may be sent to fill old quarry pits or a nearby valley). Not all the waste produced can be converted into by-products; a large quantity must still be disposed of. If the works is located near the sea, on a lake, or near a very large body of water it is a comparatively simple matter, but inland this waste can only be sent to a pond to settle, from which only the clear portion is allowed to run out to the river. The lime content in the waste liquor is particularly harmful to the fish in the river. This waste disposal must receive consideration in the selection of the site.

The foremost problem is to find an area where potential market and the present delivery costs of alkali are attractive and at the same time reasonably near sources of the necessary raw materials and fuels. Facilities for adequate and rapid service to customers eventually must be provided. This requires that a number of good transportation facilities be available (actually or potentially) in the area, for ocean, rail and motor highway movements of products. Within such an area, the few specific locations where the foregoing are favorable must be rated quantitatively on the basis of many factors. The following detailed consideration may govern the choice of the site and are given here as a resume:

(1) Delivered cost, quality and potential continuity of main fuel supply.

(2) Delivered cost, quality and assurance of an alternative or emergency fuel supply.

(3) Delivered cost, quality and reserves of limestones available.

(4) Delivered cost, quality and reserves of salt supply.

(5) Total freight cost of all products to present and potential consumers.

(6) Temperature, quantity, and chemical properties of cooling water supply.

(7) Treatment cost and treatment results of best and second best boiler feedwater supplies.

(8) Cost of solid waste disposal in near and distant future.

(9) Cost of liquid waste disposal procedure.

(10) Soil-bearing capacity and character and cost of land.

(11) Availability, intelligence and character of labor.

(12) Adequacy of housing, schools and other living facilities for personnel and workmen.

(13) Cost, adequacy and assurance of ammonia supply.

(14) Cost of coke and availability of crude ammonia liquor supply.

(15) Flood, hurricane, earthquake, etc. hazards.

(16) Cost of space for expansion or growth.

(17) Potentialities or incentive for location and growth of alkali-consuming industries.

(18) Attitude of adjacent communities toward large-scale industry.

(19) Adequacy of mill-supply and mechanical services.

In what follows we shall elaborate these points in greater detail. It is necessary that expert engineering judgment be exercised in weighting factors such as listed above relative to one another, and in computing or estimating the rating of each of the prospective sites. Since fuel, limestone and salt are the three main requirements, the selection of a site will be governed by the quality and mining cost of those which are available within the territory considered. Some of the factors which require consideration are further elaborated in the following:

The quantity and kind of fuel required have been discussed in Chapters XXII and XXVI In this chapter it need be pointed out that ammonia soda plants can burn any kind of fuel so long as it is cheap. Fuel equivalent to half a ton of high-grade coal per ton of soda is near the minimum consumption for all purposes in the direct manufacture of soda by the ammonia process. A small amount of the fuel will be burned in preparing the lime. Almost invariably this must be metallurgical coke, which is a standard commodity with a standardized market, but can conceivably be very expensive. Such is quite unlikely to be the case in any territory having a high alkali market, but is true with certain alkali plants on the Gulf Coast. A somewhat larger amount of the fuel will be required in soda dryers, and this may be bituminous coal. Since most of the fuel is used in the generation of steam, the fuel problems in selecting a site are much the same as for any other industry. These were discussed in Chapter XXII, and hence will not be dealt with here.

Continuity of operations, important as it is to economical production and high quality product, requires either very large stocks of fuel and raw materials, or assured emergency or "second-string" supplies. A combination of the two is usual. This is more important with fuel than with limestone or salt, for the latter are usually under the control of local management. The second-string fuel supply can be more costly if it is dependable.

It is decidedly advantageous that the production of salt and limestone be under the control of the soda ash manufacturer, as is generally done. That is, one department of the works should be in charge of the brine field operation and another in charge of the quarrying and prepara-

tion of the stone. Not only must sources of these raw materials give assurance of long-time inexpensive supply, but their quality must also fulfill certain requirements. This is particularly important with limestone, as is discussed in Chapter VI. Likewise an impure brine or high-magnesium sea-salt introduces added costs, as discussed in Chapters IV and V. The adequacy of each on the basis of the principles mentioned must be exhaustively considered in selecting an ideal site.

More than eight tons of brine, stone and fuel are handled into the works per ton of soda ash shipped out; and more than 12 tons, per ton of chemical caustic shipped out. On a strict ton-mile basis, therefore, the plant should occupy a position considerably nearer to its raw materials than to its market. However, about 60 per cent of the raw materials are very cheaply transported by pipe line, and freight rates on stone and coal are cheaper than on finished products like soda ash and caustic soda Furthermore, there are local discontinuities in freight rates which prevent setting up a "formula" for finding the site of minimum transportation costs. A finite (and small) number of potentially good sites can be determined by a rapid qualitative consideration of the most important factors. For these and the few suitable raw material and fuel sources, an experienced engineer should compute actual annual transportation costs based on previously prepared market estimates.

The question of cooling water supply is of considerable importance. If during the months of warm weather, no reasonably cool (ten to fifteen degrees below wet-bulb temperature) water is available, the production of the plant will suffer. Furthermore, the power required for circulating excessively large volumes of water is considerable. If a site affords a large volume of water which gets quite warm (approaches wet-bulb temperature) in the summer time, it is necessary to investigate the possibility of a supply of artesian well water for summer operation. Equipment for refrigeration of water will, under certain conditions, compete with deep-well water if the latter is scarce. Exhaust steam is suitable as the source of power for such refrigeration and is thus a sort of summer complement to the winter space-heating load. Only a small portion of each unit of cooling apparatus needs to be supplied with refrigerated water. Besides the temperature of the cooling water, it is necessary to investigate its behavior in cooling equipment. Certain waters contain temporary hardness or other solids which deposit difficultly removable crusts on cooling surfaces. Many sources of water are conducive to algae-growth in warm weather when the plant can least afford any impeded heat transfer. Others have properties of causing corrosion of metals of construction in the cooling apparatus. So it may be necessary to give the cooling water a suitable chemical treatment. This has been dealt with at great length in Chapter XXIII.

An additional supply of water may be desirable for steam generation. As mentioned before, frequently a source of excellent cooling water is a poor source for boiler feedwater. Organic contamination in this course of water is not so harmful as in the cooling water, but scale-forming solids

in solution would bring about high operating expense. Since the supply of boiler feedwater should (for best fuel economy) be given as much preheating as possible from sources of low-pressure waste heat, it must also be considered as a cooling medium. The quality of the contemplated source of feedwater, both from the standpoint of behavior in cooling equipment and from the standpoint of adequate treatment to inhibit scale forming and boiler corrosion, must be given very careful consideration. Alkali engineers generally employ water specialists on this problem.

The difference between the quantities of raw materials and finished products mentioned above must be disposed of as solid, liquid and gaseous wastes. There should be a large area adjacent to the plant for the disposal of the solid wastes, as mentioned above. These come from the distiller blow-off, the lime caustic mud, the boiler ashes, the slaker rejects, etc. This is one of the most serious problems connected with an alkali plant. The physical character of most of these solids is such that they are very poor material for land fills. The caustic mud contains excess lime. The distiller waste does not dry or harden over long periods of time. There is sufficient free lime and chloride in it so that vegetation will not grow on it for many years. Consequently the deposits are considered unsightly by most people. It cannot be disposed of in the usual rivers or public waterways. A proper site for an alkali plant should have available a large area of swamp or marsh land or valleys, which can be cheaply diked or dammed to make room for the waste disposal for a number of years. The boiler ashes and the slaker rejects may be utilized in road making for a country community.

All alkali plants have to dispose of large quantities of calcium chloride. For plants located on the seacoast, once the distiller blow-off has had the solids settled from it, this presents no problem. Inland plants, however, are faced with a difficulty caused by the introduction of the chlorine into the irrigation waters of the district. An alkali plant must therefore be located within reach of a reasonably large stream so that the chloride to be disposed of does not add appreciably to the salinity of the river water.

As explained above, most of the buildings in an alkali plant are unusually tall. Consequently unusually heavy foundation loads are encountered under the buildings as well as under the taller equipment. If an alkali plant is not located on good ground, the foundation costs may be exorbitant. Furthermore, large foundation masses inhibit pipe tunnel, elevator pit, and similar features of design, which add to the cost of the entire plant. There should be an adequate, reasonably level area and sufficiently high land for quick drainage of rainfall. The site should avoid regions of congestion and high land values.

Modern ammonia soda plants use relatively little labor, compared to most other industries, measured either per dollar of investment or per ton of the output. The usual complement of skilled maintenance artisans employed on apparatus and building repairs is required, as in most other plants. The labor for handling and loading the finished product is like-

wise the same in quantity and quality as in other industries, having a comparable division between bulk and package shipments. In direct production, however, one painstakingly trained and intelligent operator can, because of the continuity and automatic control in the operation, attend an exceptionally large amount of apparatus. Abnormalities of operation occur so seldom that it takes a long time to gain direct experience. Consequently "steady" workers are demanded. Pay rates must be such as to avoid high turn-over of labor. The incentive of a clear and substantial route of promotion for operating personnel must be "built" into the plant organization. Certain communities afford a larger market for the steady type of workers, and these must be kept in view in the selection of the site, as labor problems should not be allowed to interfere with the continuity of operations.

If housing, school and living facilities are not available in the vicinity of a favored plant site, such site must be penalized to the extent of adding the cost of such facilities to the first cost of the venture. In America, the operation of such facilities introduces additional management burdens. However, it behooves the management to provide housing facilities on a cooperative basis.

Ammonia in the form of crude coke-oven liquor must generally be contracted for, since it is hardly a commodity with a standardized market availability. Since synthetic ammonia, as anhydrous liquefied gas in tank-car lots, has become cheaper, the availability of ammonia from coke-ovens is no longer so important to a prospective alkali plant as it was 15 years ago. It was a widespread practice before the first World War (1914-1918) for alkali manufacturers either to operate their own by-product coke ovens or to locate near a by-product coke plant Today, as a matter of fact, the combination of the alkali industry with the synthetic ammonia industry has been worked out very advantageously to the ammonia soda industry.

When anhydrous ammonia is being used, the consumption of sulfur will be much higher. Although the quantity of sulfur in any case is small, the unit cost can be quite high, as was pointed out in Chapter XXVI. Since the quality of the product is quite seriously dependent on the sulfur control, this item should receive due consideration. However, where good coking bituminous coal is available in abundance, the problem of fuel, of coke, of ammonia, and of sulfur required will be once and for all solved together, when a suitable site has been selected.

Flood, hurricane, and such *force majeure* characteristics of sites should be compared on the basis of insurance rates and probability of lost production based on known history. The elevation of the ground and the design of the buildings should take into consideration the highest flood level and the maximum wind pressure likely to be encountered. Such special provisions are noticeable in the construction of certain alkali plants on the Gulf Coast.

The alkali plant site should leave room for growth. Not only can the main products be expected to increase at a reasonable rate, but also

it is reasonable to expect that by-products or end-products will be developed to the point of finding profitable production immediately adjacent to the main works. That land is preferred which permits a layout of the original plant for a methodical growth without introducing undue expense in the piping and handling of materials. Ultimate plant layout should be visualized also from the operating and maintenance standpoint.

An alkali plant serves a number of major industries. The consumer products, for which alkali is a large-scale raw material, are glass, soap, rayon, paper, petroleum oil, etc. The choice of a site for a new alkali plant must consider the proximity of the other raw materials required for the alkali-consuming industries. For example, if two sites are very nearly equal in all other respects, but one of them is reasonably close to sources of glass sand and the other is not, the former would certainly be the favored location, since it would double the incentive for the location of a glass plant adjacent to it.

An alkali plant causes no severe industrial hazards such as the fire hazard connected with a petroleum refinery or the explosion hazard of a powder works. It is not particularly malodorous, dusty or smoky. Nevertheless, it has chimneys and machinery noises to which some communities object. It has accumulation of wastes. Inordinate local taxation or other forms of burdensome legislation may be found in a community unsympathetic to this large-scale activity.

The most carefully planned and operated plant supply stores occasionally run out or fail to stock sufficient maintenance materials of great importance. The store stock also represents a large share of working capital. Some sites, therefore, have considerable monetary advantage in being close to a favorable market for factory and mill supplies. Likewise ready availability of services of specialists like gas compressor experts or large foundry and machine shop facilities is a decided asset in the assurance of lower operating costs.

As was explained in the preface and has been repeatedly emphasized in the text. this book is not intended to replace the services of a consulting engineer or an expert alkali plant designer. Before the consideration of a new alkali project has advanced beyond the preliminary market and raw material studies, capable engineering talent should be engaged to criticize such studies and later to secure the best possible plant site, plant layout and design.

In the foregoing discussion one factor has not received consideration. This may have a momentous bearing and may exert a great influence on the decision to be made, as far as plant location and the method of construction are concerned. It may be that this single factor will outweigh all others. This single factor is that of air-raid protection. When air-raid precaution is to be considered, a great many of the orthodox provisions for an ammonia soda plant layout may have to be discarded. As long as aerial warfare remains one of the vital means of military attack, no country can afford to ignore its potential menace. The principle

involved in the grouping of the various divisions of the works, in the sequence of operation, in the interrelation among the various steps in the process, in the convenience of having close proximity of one product to the next step where it is to be further processed, in the relationship between the raw materials and finished products—all these may, in part, have to be re-examined and modified. For instance, instead of locating the buildings close to one another or in rows parallel to one another in a regular formation, they may have to be scattered far apart and placed irregularly. The buildings themselves may have to be arranged and constructed just in a certain way. This will be appreciated when we bear in mind that an ammonia soda plant has many a tall building which might readily become a target from the air, and that the ammonia soda industry is strictly one of the defense industries of a nation. However, it has not been considered wise to include this in the above discussion except to mention that air-raid protection will and must receive due consideration in the location, design and construction of the ammonia soda plants of tomorrow.

Chapter XXXI

Centrifugal Pumps Applied to Ammonia
Soda Industry

The ammonia soda industry is unique in that large volumes of liquor have to be handled in the process: one of its most important raw materials —salt—is used in the form of brine, approximately 200 cu. ft. of which are required per ton of soda ash made. Besides brine, other liquors are handled in the distiller and column operations in even large quantities. Further, very large amounts of cooling water are also required and distributed throughout the plant. It is no surprise to find that centrifugal pumps are used extensively everywhere in an ammonia soda plant. Centrifugal pumps today have been brought to such a stage of perfection that they are applicable to a great multitude of services— from handling suspensions, such as milk of lime, sludge liquor, etc. to handling solutions, such as ammoniated brine, filter liquor, etc., and from pumping feed-water to boilers against a high pressure to supplying cooling and scrubbing water at moderate or low heads. Indeed, centrifugal pumps are applicable to all services in an ammonia soda plant except where a comparatively small volume of liquor is delivered against a very high head, where probably a plunger type pump may be more economical. Today large units of centrifugal pumps may have 86-88% of mechanical efficiency.

Centrifugal pumps are of two main types—the turbine type and the volute type. The turbine type is one in which diffuser vanes are incorporated in the casing to guide the flow of the liquid as it emerges from the impeller, so as to convert as much velocity head as possible back to pressure head. It is the reverse of a water turbine, although, as commonly constructed today, the vanes in the runner or impeller are curved in the opposite direction. The volute type has no vanes in the casing but depends upon a spiral-shaped chamber to guide the flow and to convert the velocity to pressure. Today, very few turbine type pumps are made except in multi-stage, high-head pumps, and by far the majority of the centrifugal pumps used in the ammonia soda plant are of the volute type because of their simplicity of design and low first cost. In what follows, we shall therefore confine our attention to the volute type pumps. (See Fig. 132.)

Centrifugal pumps may be classified as single-stage or multi-stage, according as one or more impellers are used on the same shaft. They may be single-suction or double-suction, according as the liquid enters the impeller from one side only or from both sides. They may be horizontal

or vertical, according as the impeller shaft is in a horizontal or vertical position. The vertical pump is also known as the vertical submerged pump, with the pump casing totally submerged in the liquor and the motor or turbine vertically above it. Such vertical pumps are frequently used for pumping sump tanks, or pits, or underground storage tanks. One special type of vertical pump is the deep-well pump capable of pumping liquid (underground brine or oil) up to 500 ft. depth below surface with a large number of impellers. But these are generally turbine-type centrifugal pumps with impellers of comparatively small diameter in the casings (bowls) and with diffuser vanes turned axially upward to reach the suction of the next bowl above. Because of limitation of the well bore, the impeller diameter must necessarily be kept

IMPELLER

DIRECTION OF ROTATION

VOLUTE CASING
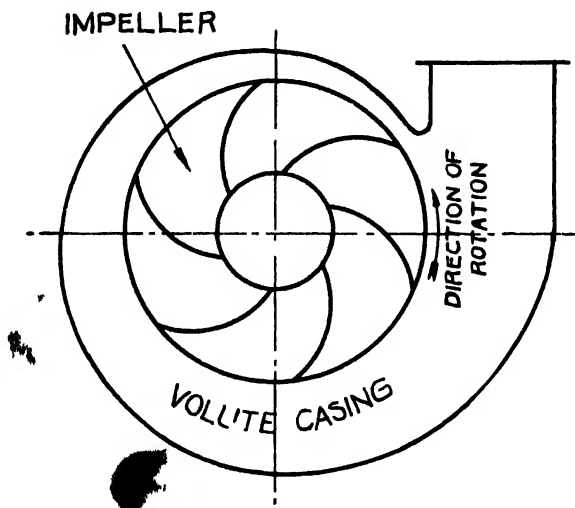
FIG. 132   Centrifugal pump, volute type

small. To obtain the head required, as many as 30 stages are not infrequently employed.

The impellers may be classified as enclosed or open, depending on whether or not the impeller vanes are shrouded on both sides. Impellers may be further classified as forward-discharge, backward-discharge, or radial-discharge, according to whether the vane tips turn toward or away from the direction of rotation, or are straight radially (Fig. 133). As may be seen below, a forward-discharge impeller has the tendency to overload the pump or increase its head, as the discharge is increased, and so is not commonly used. A radial-discharge impeller has no such tendency and generally maintains a constant head, regardless of the discharge. This type of impeller is sometimes used in high-head pumps. A backward-discharge impeller, on the other hand, generally causes a drop of head as the discharge increases, and is the one most generally
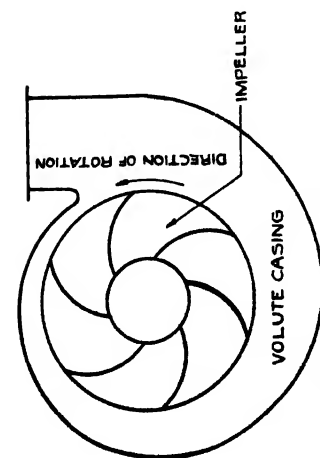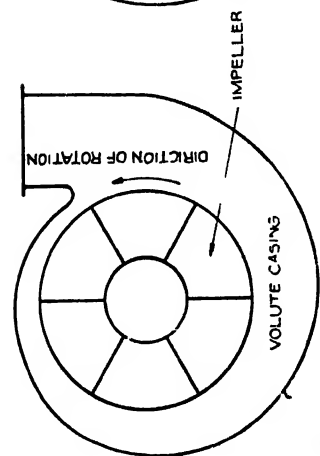
1. Backward-discharge impeller　　2. Radial-discharge impeller　　3. Forward-discharge impeller
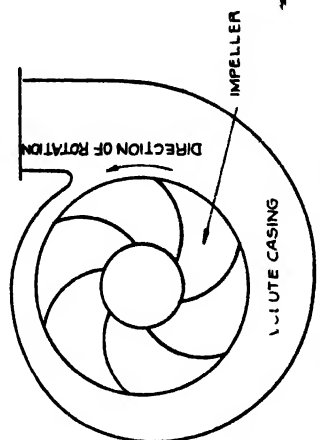
133. Centrifugal pump, volute type.

used. These statements hold only generally, because there are other factors influencing the ultimate characteristics of the pump.

An open-impeller centrifugal pump has generally only one suction on one end of the shaft opposite to the drive, the liquid entering axially from that end. Open-impeller pumps are used to a certain extent in soda plants for sludge-laden or scale-forming liquors for the following reasons:

(1) greater passage space for liquor through the impeller;
(2) simplicity and low cost of manufacture;
(3) ability to handle suspended solids, crystals or mud;
(4) ease in cleaning when the impeller is clogged or has scale built on it;
(5) one stuffing box or one source of leakage only.

Open-impeller pumps with a single suction at the end are now built integral with the motor frame with the impeller mounted on the motor extended shaft, such as "Motorpump" made by the Ingersoll-Rand Co. and "Close-Cupld" pump made by Goulds Pumps, Inc. This construction is strong, compact, and rigid with no possibility for the pump and motor to get out of alignment. Further, it is possible to turn the volute casing so as to set the discharge nozzle at any position desired.

Recently, in order to avoid leakage of corrosive liquors through the packing gland around the pump shaft, an open-impeller, single-suction centrifugal pump without any stuffing box has been perfected and placed on the market, such as that made by A. R. Wilfley & Sons, Denver, Colorado, and a vertical pump made by Allen-Sherman-Hoff. This is specially adapted to the handling of corrosive acids, chemical liquors, slurries, slimes, sandy sludges, etc. In the case of the Wilfley type pump, when the pump is running, an "expeller" by its centrifugal action prevents leakage of liquor around the shaft. When the pump is not running, a governor attached to the motor draws the pump shaft back by its spring action, closes the clearance around the shaft by a conical seal ring, and stops any leakage.

On the other hand, open-impeller pumps have lower head and lower hydraulic efficiency than enclosed impeller pumps. In all cases, where liquid in question is clean and clear, and is to be handled in large volumes at a considerable head, a double-suction, enclosed-impeller (instead of open impeller) pump is preferred, because here power saving will be an item. An open-impeller pump with a single suction at the end is not balanced, the axial thrust being toward the suction end. An enclosed impeller with double suction may be looked upon as two single open impellers placed back to back with two inlets on opposite sides, and is therefore essentially balanced. Besides, the shroud serves to guide the flow through the impeller more accurately. Hence an enclosed-impeller pump has a higher head and greater efficiency than an open-impeller one.

Compared with reciprocating pumps, centrifugal pumps have no valves, have only one moving part, and are light in construction. They

are self-balanced, so that only a light foundation is necessary. They have a large capacity per unit weight and consequently a low first cost. They may handle considerable solids in the liquid with immunity, and will not cause any accident if the delivery valve happens to be completely shut. Unlike a piston pump, a centrifugal pump cannot stand much leakage of air at the intake or around the packing glands, and must be primed to start the operation. Hence it is general practice to place the pump below the liquor level wherever possible, *i.e.*, flooded suction.

A single-stage enclosed-impeller pump can operate efficiently at a head from 160 to 180 ft. runing at 1800 or 3600 r.p.m. with not too large an impeller. The overall efficiency may be from 80-83 per cent. For a high-head service, better efficiency is obtained with a small impeller diameter and a high speed (r p.m), than with a large impeller diameter and a lower speed. The reason is that the rotation loss, due to spinning of the impeller in the liquid, varies as the fifth power of the diameter of the impeller, whereas it increases only as the cube of the speed (r.p.m.).

The number of the impeller vanes or blades is usually 6, and may vary from 4 in small ones to 8, 10 or more in large ones. Too few blades or vanes in the impeller cause insufficient guidance to the flow of the liquid through the impeller, while too many blades may restrict the liquid passage and cause excessive friction losses to the flow. In very large impellers, sometimes half vanes are provided near the periphery between two adjacent full blades. This virtually doubles the number of the impeller vanes, and improves the hydraulic efficiency, but without much increase in friction losses.

A centrifugal pump has the following five items to be considered:

(1) Head
(2) Speed
(3) Capacity
(4) Brake Horsepower
(5) Efficiency

A head-capacity curve is shown in Fig. 134.

The highest head corresponding to no discharge is the so-called "shut-off" head. As the discharge increases from zero, the head generally falls. Sometimes, as the discharge increases from zero, the head first rises and then falls. Sometimes also the head at first remains practically constant and then falls sharply as discharge is further increased. A pump is said to have a rising, flat, or falling characteristic according as the head rises, remains practically constant, or falls, as the delivery valve opens from the shut-off position. A falling characteristic curve is again referred to as "steep" or "flat," depending on whether, when the head decreases, the capacity increases slowly or rapidly. Services where more or less constant discharge is required favor the steep characteristic type of pump. It is generally true that a forward-discharge impeller has a rising characteristic, a radial-discharge impeller a flat characteristic, and a backward-discharge impeller a falling characteristic, although

sometimes backward-discharge impellers may have a distinct rising characteristic (see below).

A centrifugal pump is essentially a high-speed rotative machine adapted to be direct-connected to an electric motor or a steam turbine, although a belt drive, such as V-belt drive, is often used. If the pump is driven by a steam turbine, the speed may be changed as desired; but if it is direct-connected to a squirrel-cage motor, it is essentially a constant-speed machine. The brake horsepower (b.h.p.) generally increases
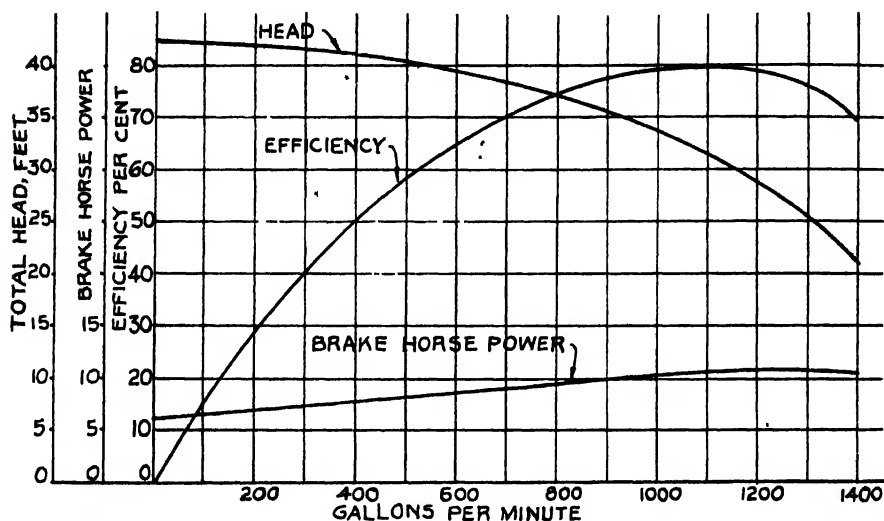
Fig. 134.   Performance curve of a centrifugal pump.

as the head decreases and the discharge increases. The rated capacity is generally chosen at a point of maximum efficiency on the head-discharge curve, or at a little beyond that, and is known as the rated, or full-load, capacity. At zero discharge (or shut-off position) the horsepower required may be only 20-40 per cent of the full-load brake horsepower. At a head lower than the rated, the discharge greatly increases, and the pump may require a much greater power for drive—so much so that a constant-speed motor driving the pump may run dangerously hot at a low head and high discharge, especially if the pump happens to have rising characteristics. It is generally desirable so to design the impeller that the b.h.p.-capacity curve is almost flat or slightly increasing to a maximum, then decreasing rapidly. Fig. 134 shows the head-capacity, b.h.p.-capacity, and efficiency-capacity curves of a backward-discharge, single-stage, volute pump.

The b.h.p. is determined by a dynamometer, and the discharge is generally measured by a nozzle or an orifice between pipe flanges. The suction and delivery pressures are measured by a mercury manometer and a pressure gauge respectively. A piezometer gauge attached to

the nozzle determines the volume of discharge for a standard nozzle. When an orifice is used, a differential manometer is required. The output of the pump is:

$$\text{Liquid h.p.} = \frac{HQs}{33,000} \times 8.33 = \frac{HQs}{3960},$$

where
H = head in ft.
Q = discharge in gal. per min.
s = sp. gr. of the liquor.

or
$$\text{Liquid h.p.} = \frac{144\,PQ \times 8.33}{62.4 \times 33,000} = \frac{PQ}{1715}.$$

where
P = pressure in lbs. per sq. in. (ga.)

The second formula does not need the specific gravity of the liquor being pumped. This is the pump output. The input is measured by a dynamometer giving

$$\text{b.h.p.} = \frac{WR}{12} \times \frac{2\pi N}{33,000} = \frac{WRN}{63,000};$$

where
W = lbs. on the dynamometer scale
R = length of knife-edge arm in inches
N = r.p.m.

This is the input which may be further checked by the voltage and amperage of the dynamometer motor when its efficiency is known:

$$\text{b.h.p.} = \frac{\text{volts} \times \text{amp.} \times \text{efficiency}}{746}$$

The efficiency of the pump is

$$e = \frac{\text{liquid h.p.}}{\text{b.h.p.}} \times 100\%$$

The efficiency of a pump of moderate size nowadays is as high as 80-84 per cent or more. This efficiency increases as the discharge increases from zero, because at a low discharge, the output is small and the mechanical and hydraulic losses constitute a big item in the input. The efficiency then gradually rises to a maximum as the pump is brought to the rated discharge. But beyond this point, the efficiency drops again, because at a high rate of discharge beyond a certain limit, high velocity of the liquid at the entrance to the impeller causes excessive drop in pressure, resulting in a high vacuum and consequently in the vaporization of the liquid, rarefaction, or cavitation. This causes high consumption of power without commensurate increase in the discharge. Therefore the efficiency finally falls sharply, and discharge reaches a figure which it cannot exceed even if the head drops to zero.

As mentioned above, at the rated capacity, the b.h.p. may not be at its maximum, but may continue to rise in spite of the fact that the head is rapidly falling. When the pump is direct-connected to a constant-speed motor, it is advisable to use a motor with its rated h.p. not merely large enough to drive it at the rated capacity, but large enough also to take care of any increased power required when the pump happens to be

operated at a lower head than the rated and consequently at an increased discharge; otherwise the motor then might be dangerously overloaded. Especially is this so in an ammonia soda plant where most of the liquors form scale in the pump and on the impeller, and where the liquors pumped may contain a certain proportion of crystals. This demands an increase in power in the pump operation and so generally a 40° C. rise motor is preferable because of its 15 per cent service factor.

For the benefit of the operatives in the ammonia soda industry, we shall now discuss in more or less detail the relationship between the speed, size of impeller, head, capacity, brake horsepower, and efficiency of a centrifugal pump. These statements will apply mostly to the backward-discharge, single-stage, volute type, horizontal centrifugal pumps.

A. **Effect of Change of Speed.** If the r.p.m. of a centrifugal pump are increased (say by a change of the motor or steam turbine speed), the peripheral speed u_2 of the impeller is increased proportionately. As the shut-off head $h_0 = \dfrac{u_2{}^2}{2g}$, the head increases as the square of the r.p.m. To maintain the same efficiency, the relative velocity of the liquid, v_2, through the impeller must be proportionally increased. Since the discharge Q is directly proportional to this relative velocity, the cross-section of the impeller passage remaining constant, the discharge increases directly as the r.p.m. Since power is the product of the head into discharge per unit time, power required increases as the cube of the r.p.m.

B. **Effect of Change in Impeller Diameter,** other dimensions remaining constant. The increase in the impeller diameter, D, proportionally increases the peripheral speed of the impeller for a given r.p.m. Therefore the relationship given above applies here. The general practice with centrifugal pump manufacturers is to adopt, within a limited range, a certain size of volute casing capable of being fitted with any of the several sizes of impellers of the same pattern, but differing in the outside diameters. This leaves different space in the volute chamber for free vortex. Also, a change in the diameter of the impeller sets up a new condition in the passage of the liquid through the impeller. Thus, the relationship

$$h_0 \propto D^2$$
$$Q \propto D$$
$$\text{b.h.p.} \propto h_0 Q \propto D^3$$

will hold approximately. Therefore, to meet the' requirements in the head desired when the discharge required is very small, it is sometimes necessary to go into the extreme impeller diameter, if the r.p.m. can no longer be increased. Here the friction losses due to disc rotation increase rapidly with increase in the impeller diameter, and so high-head pumps that require excessively large impeller diameter for a limited volume of discharge necessarily have lower efficiencies.

C. **Effect of Change of Impeller to Another in Homologous Series.** In a homologous series we have a family of impellers each having the outside diameter, the diameter of the "eye," the width of impeller, the

cross-section of liquid passage, the space in the volute chamber, the curvature of the vanes—all in geometrically similar proportions. Let D = impeller diameter in inches, N = r.p.m.. Q = discharge in gals. per minute. Then

$$h_o = \frac{u_2^2}{2g} = \frac{\left(\frac{D}{12} \cdot \frac{\pi N}{60}\right)^2}{2g} = \left(\frac{DN}{1840}\right)^2 \text{ approx., and}$$

$$Q = \text{cross-section of impeller passage} \times v_3$$
$$\propto D^2 \times D$$
$$\propto D^3$$

Therefore the shut-off head increases as the square of the diameter of the impeller for a given N, and the discharge increases as the cube of the diameter. Consequently the power required increases as the fifth power of the impeller diameter at a given r.p.m.

$$\text{b.h.p.} \propto D^2 \times D^3$$
$$\propto D^5$$
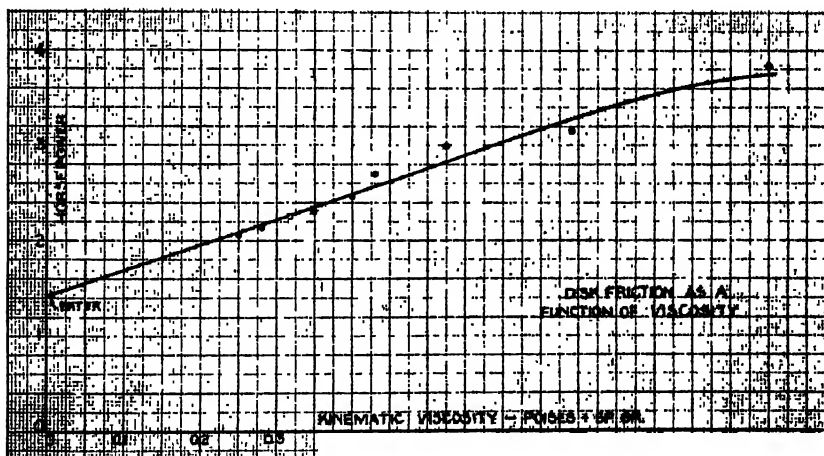
Fig. 135. Disk friction as a function of viscosity.

D. Effect of Change of Specific Gravity of Liquor. The liquid h.p. as given above equals $\dfrac{HQs}{3960}$. Therefore, other conditions being equal, the power required increases directly as the specific gravity. Contrary to the common belief, the head of a centrifugal pump is independent of the specific gravity of the liquid, provided the change in specific gravity is not accompanied by a change in viscosity. A centrifugal pump rated at 100 feet head on water will develop the same head when it is pumping brine (specific gravity = 1.20) or strong sulfuric acid (specific gravity 1.84), making suitable allowance for the increase in viscosity, provided there is sufficient power in the motor to develop the same r.p.m. And

this demands greater power. Further, the power required is actually greater than corresponds to the specific gravity because of greater friction losses due to more viscous liquid. Also, the discharge would not be affected by a change in specific gravity, provided the viscosity remains substantially the same.

E. **Effect of Change of Viscosity of Liquid.** The increase in viscosity greatly increases friction losses in the suction pipe, the impeller, the volute chamber, and the delivery pipe. The effect, however, is rather complicated and cannot be simply formulated. An insight may be gained from the manner that this viscosity factory μ is involved in the Reynolds Number $\dfrac{Dvs}{\mu}$ (where $D =$ diameter of conduit in feet, $v =$ relative velocity in feet per sec., $s =$ specific gravity, and $\mu =$ absolute viscosity in poises). Friction factor increases as the Reynolds Number decreases and so the larger μ is, the smaller is the Reynolds Number, and the greater is the friction. In general, increase in the viscosity of the liquid causes decrease in the head, in the capacity, and in the efficiency, and increase in the disc friction (see Fig. 135) and in the power required.

However, Prof. Daugherty * found that for small increase in viscosity, varying from 31 sec. (Saybolt Universal Viscosimeter) for water to 70 sec. for light crude oil—absolute viscosity varying from 1 to 10 centipoises—the characteristic head-capacity curve of the pump was not materially affected. However, a larger increase in viscosity would cause a steep drop in the head-capacity curve of a pump, and a considerable reduction of the maximum efficiency point on the efficiency-capacity curves; and this effect is more marked for small pumps than for large ones. For the same reason, increases in viscosity cause a larger percentage decrease in efficiency, capacity, etc. in a small pump than in a large pump. Further, the increase in viscosity affects the behavior of the liquid in the impeller passage and in the volute casing so fundamentally that the same pump designed originally for maximum efficiency on water may not operate most efficiently on viscous liquids such as heavy oils. It seems that for heavier oils whose viscosities are much higher, an impeller having a somewhat larger vane angle will operate more efficiently.

F. **Effect of Change of Suction Lift,** other conditions remaining unchanged. Increase in partial vacuum or suction at the pump intake causes marked decrease in discharge at low heads where very high discharge is normally expected. On the contrary, at high heads or with the delivery valve throttled to reduce the volume of discharge, normal head (or identical characteristic head-capacity curve) then is obtained. How small this discharge should be throttled to, in order to maintain the

* "Investigations of the Performance of Centrifugal Pumps When Pumping Oils," by R. L. Daugherty, Goulds Pumps, Inc., Bulletin 126.

"A Further Investigation of the Performance of Centrifugal Pumps When Pumping Oils," by R. L. Daugherty, Goulds Pumps, Inc., Bulletin 130.

head, depends upon the suction conditions at the intake. At 25" Hg. suction, the discharge must be reduced to less than one-half of the rated capacity before the normal head-capacity relationship can be maintained The b.h.p. required is greatly reduced at low heads, as the vacuum at the intake increases, evidently because of the decreased volume of discharge. For the same reason, efficiency of the pump generally decreases with a high vacuum at the intake. Also, high vacuum tends to draw in air at the intake or around the packing gland. Consequently, the pump will have difficulty in priming or may even lose priming during operation. To prevent leakage of air through the packing glands, pump manufacturers provide deep stuffing boxes so as to receive not less than six rings of packing material with a lantern ring in the middle of the stuffing box, into which liquid from the volute chamber may be led by connecting a small pipe, one to each side of the pump.

G. **Effect of Gases or Volatile Components in Liquid.** When the liquor pumped contains any volatile gases, such as CO_2 or NH_3 in the warm filter liquor, centrifugal pumps must not be operated at a suction. As a rule, in a soda plant it is wise to locate, wherever possible, all centrifugal pumps below the liquor level so that suction may be flooded. When a centrifugal-type feed-water pump is installed in the boiler plant, handling hot feed water from the deacrator to the boiler, a static head of the hot water column above the feed-pump suction sufficient to develop a pressure in excess of the vapor pressure of water at the temperature at which the deacrator is operated, must be provided. This may be as much as 20 feet above the pump suction. The presence of the gases in the centrifugal pump causes decrease in the discharge and in the head attained. When much gas is present, the pump fails to deliver any liquid, i.e., "loses priming." Due to the decreased volume of discharge, the power required is somewhat less, while the efficiency drops greatly. The symptom from the presence of gases in the pump is so closely connected with that from a high suction that the same remedy is resorted to, namely by throttling down the volume of discharge pending the removal of the cause of trouble. A bib-cock is provided at the highest point or "crown" of the volute chamber to vent gases, after bringing the pump to rest.

Two similar centrifugal pumps may be operated in parallel when they have about the same head. Then the discharge will be the sum of the two, but the head will be the same as that of each individual pump. This is like a parallel operation of two alternators with the same electrical characteristics. The current is increased but the voltage remains the same. When two such pumps are connected in series, the discharge of one going to the intake of the other, the capacity of the two so connected is the same as that of each, but the head is the sum of the two. These are just like a two-stage pump, each stage being a separate unit. But seldom are centrifugal pumps connected this way.

In the trade, the size of a centrifugal pump is usually designated by the diameter of the delivery nozzle. As mentioned above, the head and

capacity of the pump are chosen at the point of maximum efficiency of the pump when operating at a given speed (r.p.m.). The maximum head developed by a pump is understood to be its shut-off head when the pump just fails to deliver. A typical data sheet showing all characteristic curves of a particular centrifugal pump is shown in Fig. 136.

Centrifugal pumps are designed and fitted specially for a given speed at a maximum efficiency for a certain head and capacity. Changes in conditions of operation in the field may cause the pump to fail to attain that efficiency.
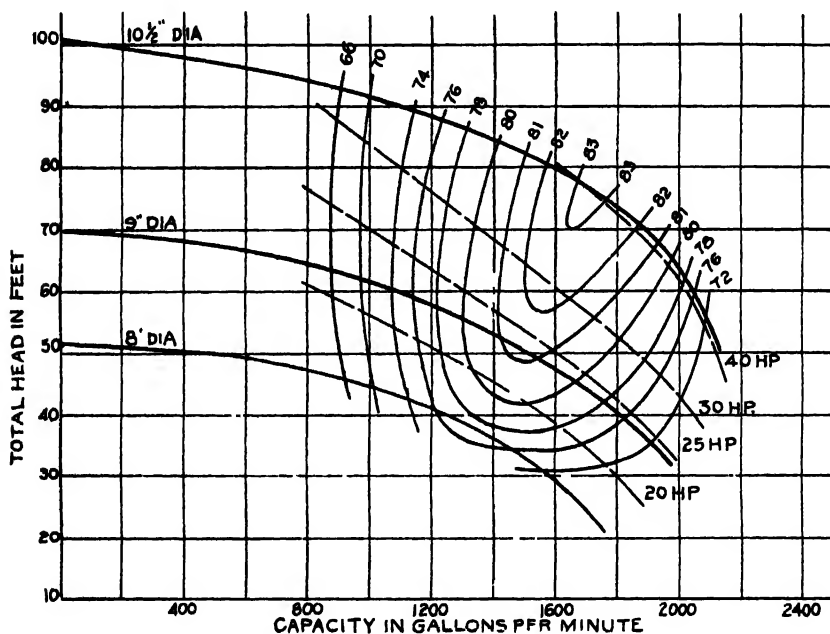
FIG. 136. Centrifugal pump data sheet.

Centrifugal pumps were known more than a century ago—in fact, Euler in 1755 propounded the theory—but real application did not begin until about 1849, when Appold in England invented the pump and introduced it into practical use. Appold was the first to use curved vanes, but the introduction of the diffuser vanes in the casing was generally credited to Osborne Reynolds of Reynolds Number fame, who built a pump with diffuser vanes in 1875. Up to this time, construction was still imperfect and efficiency very low, due to the fact that high rotative machines were at that time unavailable. Not until about the close of the nineteenth century, when high-speed turbines were perfected, was efficiency improved and the pump considered commercially applicable. In 1896, Sulzer of Winterthur, Switzerland, and about the same

time, Byron Jackson of San Francisco, Cal., began to manufacture centrifugal pumps on a large scale.

As the name implies, centrifugal pumps work on the principle of centrifugal force. The impeller, or runner, by its high rotative speed, imparts centrifugal motion to the liquid. The velocity attained by the liquid as it leaves the impeller is converted to pressure as much as possible. While pressure of a liquid may be converted into velocity readily, the reverse of transforming velocity back to pressure cannot be
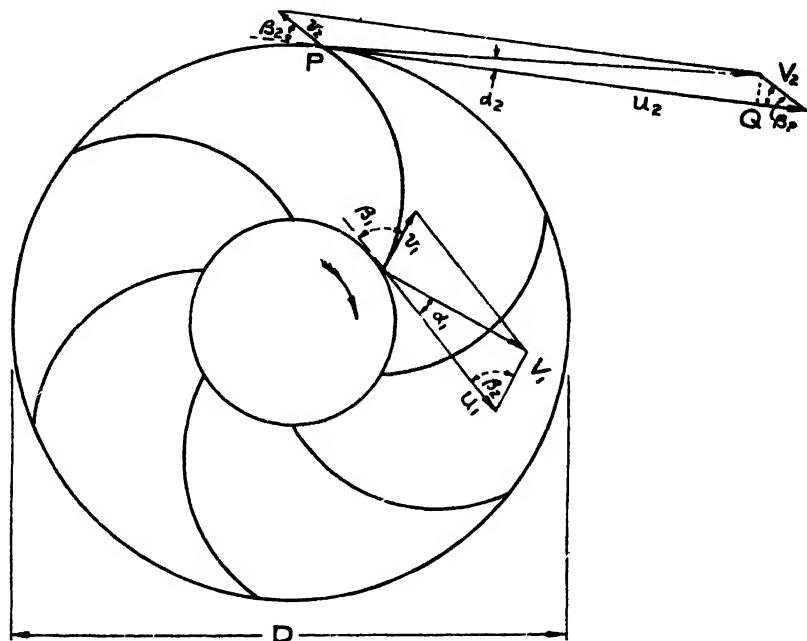
Fig. 137.

accomplished completely. Consider the impeller shown in Fig. 137 rotating in the direction of the arrow at N r.p.m. Let

> u_1, u_2 be the tangential velocities at the circumference of the "eye" and at the impeller rim respectively.
>
> v_1, v_2 be the relative velocities of the liquid with respect to the impeller at the entrance and outlet of the impeller respectively.
>
> V_1, V_2 be the absolute velocities of the liquid at the entrance and at the outlet of the impeller
>
> α_1, α_2 be the angles which these absolute velocities make with these tangential velocities respectively.
>
> β_1, β_2 be the angles which the relative velocities of the liquid in the impeller make with these tangential velocities respectively, produced in the negative direction.
>
> D be the impeller diameter in feet.
>
> W be the weight in lbs. of the liquid passing through the impeller per sec., and g gravity.

Since W lbs. of the liquid passing through the impeller per sec. and the impeller imparts to the liquid an absolute velocity V_2, the impeller is imparting to the liquid a tangential momentum $\dfrac{W}{g} \cdot V_2 \cos \alpha_2$ per sec. By the principles of mechanics, change of angular momentum (or moment of momentum) with respect to time is equal to the torque

$$\therefore \frac{W}{g} \cdot V_2 \cos \alpha_2 \times \frac{D}{2} = \text{Torque.}$$

Also,

$$\text{Torque} \times \text{Angular Velocity} = \text{Power}$$

$$\therefore \frac{W}{g} \cdot V_2 \cos \alpha_2 \times \frac{D}{2} \times \text{Angular Velocity} = \text{Power} = W h_2 \quad \begin{matrix}\text{(where } h_2 \text{ is head in ft.}\\ \text{induced by the rotation}\\ \text{of the impeller).}\end{matrix}$$

Since

$$\text{Angular Velocity} = \frac{2\pi N}{60} \text{ per sec.}$$

$$\therefore \frac{W}{g} \cdot V_2 \cos \alpha_2 \times \frac{D}{2} \times \frac{2\pi N}{60} = W h_2$$

$$\therefore h_2 = \frac{V_2 \cos \alpha_2}{g} \times \frac{\pi D N}{60}$$

But

$$\frac{\pi D N}{60} = u_2$$

$$\therefore h_2 = \frac{u_2 V_2 \cos \alpha_2}{g}.$$

In the same way, we might derive the head induced by the rotation of the impeller eye for the liquid at the entrance. Thus,

$$h_1 = \frac{u_1 V_1 \cos \alpha_1}{g}$$

And the net head developed is

$$h_2 - h_1 = \frac{u_2 V_2 \cos \alpha_2 - u_1 V_1 \cos \alpha_1}{g}$$

Since in the actual construction of the centrifugal pumps, the liquid enters the "eye" of the impeller at right angles to the plane of the impeller (or axially) and even with a whirling motion as it enters the impeller, α_1 is practically 90° and cos α_1 approaches zero.

$$\therefore \text{Theoretical head developed} = h' = h_2 - h_1 = \frac{u_2 V_2 \cos \alpha_2}{g} \qquad (1)$$

Now from plane geometry, in the parallelogram of forces we have the following relationship:

$$v_2^2 = u_2^2 + V_2^2 - 2 u_2 V_2 \cos \alpha_2$$

Solving for $u_2 V_2 \cos \alpha_2$ we have

$$u_2 V_2 \cos \alpha_2 = \frac{u_2^2 + V_2^2 - v_2^2}{2}$$

$$\therefore h' = \frac{u_2^2}{2g} - \frac{v_2^2}{2g} + \frac{V_2^2}{2g} \qquad (2)$$

In the actual operation of the pump, the liquid passing through the impeller with a relative velocity v_2 sustains some friction losses which we may put as $K_1 \dfrac{v_2{}^2}{2g}$ (K_1 being some constant). Also, as mentioned above, it is not possible to convert all the velocity head into pressure head. Call K_2 the fraction so converted. Therefore, in the actual pump, the actual head developed is

$$h = \frac{u_2{}^2}{2g} - (1 + K_1) \frac{v_2{}^2}{2g} + K_2 \frac{V_2}{2g} \tag{3}$$

Now when the pump is operating with the delivery completely cut off, or when the pump is operating against a head at a point where the flow of the liquid (or discharge) just ceases, then there is no definite flow of the liquid through the impeller, *i.e.*, the relative velocity $v_2 = 0$. Under such conditions, the liquid just spends itself with violent eddies in the volute casing, and very little of its velocity head is available for building up pressure head. Thus, the head is all due to the "whirling head" of the liquid in the pump. This means that the fraction K_2 is also practically zero. This leaves on the right-hand side of equation (3) only the first term, $\dfrac{u_2{}^2}{2g}$ which we may call the shut-off head h_0, of the pump and so we may set the actual head:

$$h = h_0 - (1 + K_1) \frac{v_2{}^2}{2g} + K_2 \frac{V_2{}^2}{2g} \tag{4}$$

and the shut-off head $h_0 = \dfrac{u_2{}^2}{2g}$. But in an actual pump, this is not exactly the case. for we find that h_0 may be from 0.85 to 1.10 $\dfrac{u_2{}^2}{2g}$.

Now when a pump is operating, as the delivery valve is opened and discharge increases from zero, the head may either increase, diminish, or remain practically constant, as it approaches its normal capacity, according as the second term is smaller than, larger than, or equal to, the third term on the right-hand side of Equation (4), or as

$$(1 + K) \frac{v_2{}^2}{2g} \lessgtr K_2 \frac{V_2{}^2}{2g}$$

This then determines qualitatively the nature of the characteristic head-capacity curve of the pump in question.

Again, from the parallogram of forces above,

$$V_2 \cos \alpha_2 = PQ = u_2 - v_2 \cos \beta_2$$

$$\therefore h' = \frac{u_2 V_2 \cos \alpha_2}{g} = \frac{u_2 (u_2 - v_2 \cos \beta_2)}{g} \quad \text{from (1)}$$

$$= \frac{u_2{}^2}{g} - \frac{u_2 v_2 \cos \beta_2}{g} \tag{5}$$

Here β_2 is the vane angle of the impeller at its periphery.

For a given speed (N r.p.m.) of the pump, u_2 is a constant. Therefore from Equation (5) the smaller the angle β_2, the larger its cos β_2 becomes, and the smaller is the head, h', that can be induced. Consequently, for a high head pump, the designer often resorts to using a larger vane angle β_2. But a larger vane angle β_2 gives rise to a larger absolute velocity V_2 leaving the impeller for a given magnitude of the relative velocity v_2, which can be shown in Fig. 138. Thus, a larger β_2 results in a higher absolute velocity, V_2, of the liquid as it emerges from the impeller. But this is disadvantageous, because the conversion of the velocity head back into pressure head is at best inefficient. The usual
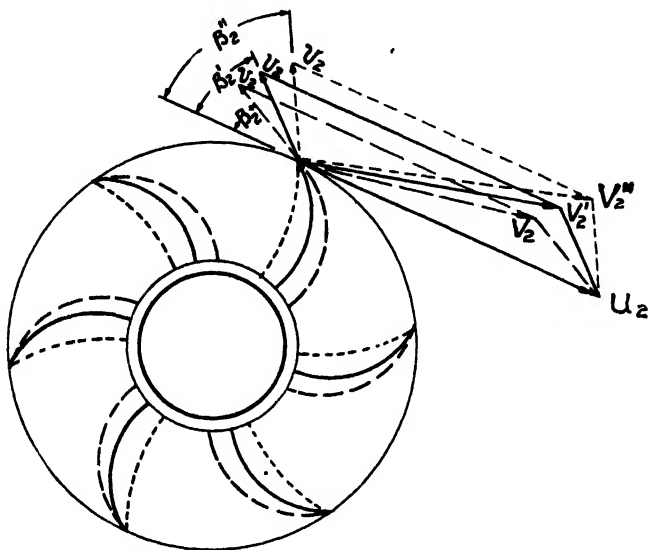
FIG. 138. Absolute velocities of liquid resulting from varying vane angles.

practice is to keep V_2 low. Therefore, the design as regards the vane angle represents a compromise. In practice, the angle β_2 is usually between 20 and 30°. Hence the impeller vane looks much like a long scroll. To go much lower than 20° is not practical, because this would seriously restrict the passage of the liquid through the impeller. Also, for a given head it would require a much higher peripheral speed of the impeller (greater r.p.m.) for the pump to develop the head required, thus incurring greater disc loss.

Now let us again consider Equation (5) in which the second term on the right-hand side appears in the negative sense. The vector quantities u_2, v_2, and g are positive. The value of h' will increase, diminish, or remain the same, according to whether cos β_2 is negative, positive, or zero. In a forward-discharge impeller, β_2 is greater than 90° and cos β_2 is negative. Fig. 133 (3). As the discharge increases from zero, approach-

ing the normal capacity, v_2 increases. Consequently, the induced h' increases. Hence a forward-discharge impeller has rising characteristics, and tends to overload the motor as the discharge increases. On the other hand, in a backward-discharge impeller, β_2 is less than 90°— generally very much less—and so cos β_2 is positive, and the head, h', tends to diminish as the discharge increases from zero. This shows how a backward-discharge pump has generally a falling characteristic. If now an impeller has radial vanes—a radial-discharge impeller—then $\beta_2 = 90°$, cos $\beta_2 = 0$, and the second term on the right-hand side of Equation (5) drops out. Consequently, in a radial-discharge centrifugal pump, the head of the pump is independent of the volume of discharge.

Hence by controlling the vane exit angle β_2 it is possible to obtain a sharply drooping characteristic for the head-capacity curve, which will not overload the motor at low head and high discharge. Generally speaking, the smaller the angle β_2, the less tendency it has to overload. Also by changing the inlet angle β_1 (Fig. 137) it is possible to obtain different efficiencies from a pump. A higher-speed pump generally requires a larger inlet angle β_1 to secure a greater efficiency. Thus it is seen that by changing these vane angles β_2 and β_1, the performance of the pumps may be altered as desired. And this is then definitely checked against test results in the laboratory.

However, these are only general and qualitative statements subject to the influence of many other factors. For instance, as mentioned above, cases are known where a backward-discharge impeller pump with a vane angle of 30° or less had a distinct rising-characteristic head-capacity curve and tended greatly to overload the motor at a low head and high discharge.

To understand these factors more clearly, we shall discuss more in detail the efficiencies and the various sources of loss in a centrifugal pump. Power is supplied to rotate the impeller at a definite speed so that the pump may deliver a certain quantity of the liquid in a unit time against a definite head. This power is called the input, and the work in lifting the liquid to a certain height against a certain pressure constitutes the output. This useful output is also known as liquid h.p. On the input side, power is supplied sufficient not only to raise a certain quantity of the liquid in a unit time to a certain height, but also to overcome (a) the bearing friction of the rotating shaft, and (b) the disc friction of the rotating impeller in the liquid. Bearing friction is generally a small item of loss, but the disc friction loss is often a considerable item, especially when the impeller diameter is large and is running at a high speed, such as in a high-head pump. This rotative disc friction consumes from 2 to 6 per cent of the total power input, while bearing and gland friction amounts to only a fraction of 1 per cent for a moderate-size pump. The disc friction for an open impeller is greater than for an enclosed impeller of the same diameter, and this is also one reason why an open-impeller pump is less efficient.

On the output side, we have (c) hydraulic friction losses, such as

friction in the passage of the liquid through the impeller caused by the rough surfaces underneath the impeller shrouds and by the rough edges along the curvature of the impeller vanes. There are also (d) eddy current losses within the impeller passage, due to the fact that the velocity of the liquid over the whole cross-section of the impeller passage is not uniform (the velocity of the liquid behind the concave side of the vane in a backward-discharge impeller being greater than that of the liquid in front of the convex side): as a result, local eddies are set up, whirling from behind the concave side of the vane to the convex side of the following vane in the passage. These eddy losses within the passage in the impeller will be better appreciated when we consider that it is mostly by this sort of action that the liquid keeps itself circulating when the pump is operating at its full speed with the delivery valve completely shut off. The total hydraulic losses for (c) and (d) above may amount to from 2 to 5 per cent. Next, as the liquid emerges from the impeller, we have (e) losses due to sudden change in the direction of the resultant velocity (or "shock" losses), which the liquid is obliged to make as it leaves the impeller. Such losses caused by a change in direction are also called diffuser losses. Also, there are some friction losses in the whirlpool chamber of the casing. Of all the individual items of losses both on the input and output sides, this single item of the diffuser loss is probably the largest. This may account for the loss of from 7 to 15 per cent of the total power input, depending upon the design of the impeller relative to the casing, and the viscosity and specific gravity of the liquid in

α_2 = DIFFUSER VANE ANGLE
= ABSOLUTE VELOCITY ANGLE
FROM IMPELLER

IMPELLER
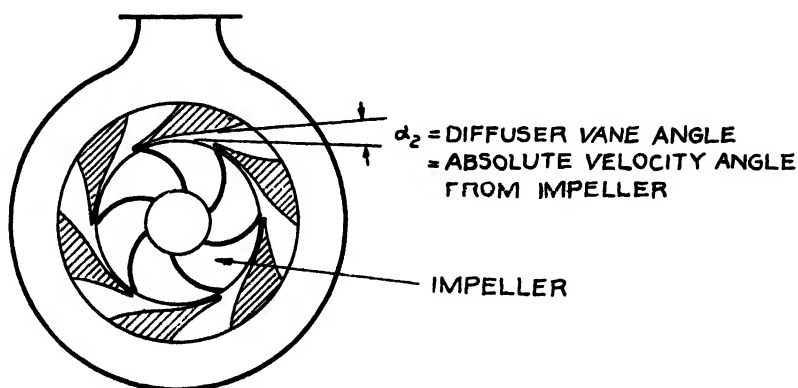
FIG. 139. Turbine pump with circular casing.

question. It is often said that while a pressure head of a liquid can be readily changed to a velocity head, the converse is not so; and by the nature of the usual construction of the pump casing with respect to the location of its outlet nozzle, such losses will be present and may be minimized but cannot be entirely eliminated. On the other hand, with a poorly designed casing, these "shock" losses may assume still greater proportions. It is to minimize these "shock" losses that diffuser vanes

are provided in the casing, in which case the angle of each of the diffuser vanes is made equal to α_2. (See Fig. 139.) For this purpose the Pomona Pump Company, Pomona, California, have developed a type of "bulbous" vane end shape for the diffuser vanes to give the streamline effect (see Fig. 140). It is claimed that by the use of this bulbous shape to guide the flow of the liquid in the casing, the efficiency of the centrifugal pump may be increased by as much as 10 per cent.
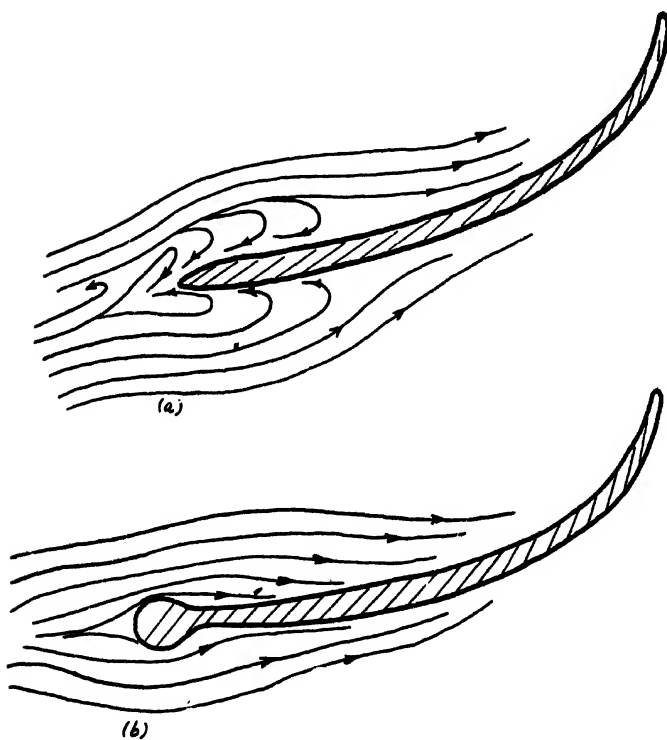
FIG. 140. Diffuser vane end shapes.
(a) Ordinary diffuser end shape.
(b) Pomona bulbous diffuser end shape.

Finally, because of mechanical difficulties it is impossible to isolate completely the suction port of the pump from the delivery chamber, and so a certain portion of the liquid under the differential pressure between the delivery and suction will find its way back to the suction around the so-called wearing ring, into which the "eye" of the impeller fits. This means that a certain amount of the liquid from the delivery side will

return to the suction, and the leakage represents just so much waste of effort. Such leakage loss (f) in a large pump constitutes only a very small item, but in a high-head pump, having a small volume of discharge, this leakage loss represents a comparatively large item of power loss. This is another reason why a high-head pump with a small capacity is not so efficient.

From the above it can be seen that efficiency of a centrifugal pump, defined as

$$\frac{\text{``Water'' h.p.}}{\text{Total Power Input}} \times 100$$

will be low, in view of the many sources of loss. Nevertheless, centrifugal pump manufacturers today have so perfected the design with a view to minimizing all these losses that in a pump of good size, an efficiency not lower than 84 per cent as mentioned above is easily attainable, even for a volute type of pump without any diffuser vanes. This may be estimated from the magnitude of losses in items (a) to (f) enumerated above.

As has been mentioned, conditions in the centrifugal pumps are very complicated. There are also opposing tendencies. Actual conditions are seldom exactly as represented in the above theoretical discussion. For instance, Prof. Daugherty of the California Institute of Technology found that the angle the relative velocity v_2 makes with the tangent was not β_2, but $4°$—$9°$ less than β_2. Again, conditions inside the liquid passage space in the enclosed impeller, bounded by the two impeller shrouds and the adjacent scrolls of vanes, are very uncertain, and so the behavior of the liquid therein may be influenced by many unknown factors. Consequently, exact mathematical relationship is difficult to establish and much still depends upon the test data.

Appendix

Some Important Tables and Curves for Reference in Soda Works

The following is a collection of some important data and curves not given in the foregoing text. They should be in the possession of men engaged in the alkali industry as they refer to the manufacture of soda ash, bicarbonate of soda, caustic soda, calcium chloride, chlorine, etc.

TABLE 163. Comparison of Commercial Soda Ash Tests in Different Countries.

Gay-Lussac Degrees % Na₂O	German Degrees % Na₂CO₃	English (Newcastle) Degrees	American (New York and Liverpool) Degrees	French* Degrees
46.50	79.50	47.11	48.00	73.54
47.00	80.35	47.62	48.52	74.33
47.50	81.21	48.12	49.03	75.13
48.00	82.06	48.63	49.55	75.92
48.50	82.92	49.14	50.06	76.71
49.00	83.77	49.64	50.58	77.50
49.50	84.63	50.15	51.10	78.29
50.00	85.48	50.66	51 61	79.08
50.50	86.34	51.16	52.13	79.87
51.00	87.19	51.67	52.65	80.66
51.50	88.05	52.18	53.16	81.45
52.00	88.90	52.68	53.68	82.24
52.50	89.76	53.19	54.19	83.04
53.00	90.61	53.70	54.71	83.83
53.50	91.47	54.20	55.23	84.62
54.00	92.32	54.71	55.74	85.41
54.50	93.18	55.22	56.26	86.20
55.00	94.03	55.72	56.77	86.99
55.50	94.89	56.23	57.29	87.78
56.00	95.74	56.74	57.81	88.57
56.50	96.60	57.24	58.32	89.36
57.00	97.45	57.75	58.84	90.15
57.50	98.31	58.26	59.35	90.95
58.00	99.16	58.76	59.87	91.74
58.50	100.02	59.27	60.39	92.52

* Equivalent to parts of H₂SO₄ per 100 parts of Na₂CO₃.

Note—This table is applicable not only to soda ash but also to caustic soda and other alkalies. For caustic soda the table should be extended beyond 58.50 % Na₂O up to 77.50%. The tendency at present is towards using the Gay-Lussac degree (% available Na₂O) which is scientifically correct (see Table 165).

TABLE 164. Specific Gravity of Sodium Chloride Solutions at Various Temperatures.*

Per Cent NaCl	0° C.	10° C.	20° C.	25° C.	30° C.	40° C.	50° C.	60° C.	80° C.	100° C.
1	1.00747	1.00707	1.00534	1.00409	1.00261	0.99908	0.99482	0.9900	0.9785	0.9651
2	1.01509	1.01442	1.01246	1.01112	1.00957	1.00593	1.00161	0.9967	0.9852	0.9719
4	1.03038	1.02920	1.02680	1.02530	1.02361	1.01977	1.01531	1.0103	0.9988	0.9855
6	1.04575	1.04408	1.04127	1.03963	1.03781	1.03378	1.02919	1.0241	1.0125	0.9994
8	1.06121	1.05907	1.05589	1.05412	1.05219	1.04798	1.04326	1.0381	1.0264	1.0131
10	1.07677	1.07419	1.07066	1.06879	1.06676	1.06238	1.05753	1.0523	1.0405	1.0276
12	1.09244	1.08946	1.08566	1.08365	1.08153	1.07699	1.07202	1.0667	1.0549	1.0420
14	1.10824	1.10491	1.10085	1.09872	1.09651	1.09182	1.08674	1.0813	1.0694	1.0565
16	1.12419	1.12056	1.11621	1.11401	1.11171	1.10688	1.10170	1.0962	1.0842	1.0713
18	1.14031	1.13643	1.13190	1.12954	1.12715	1.12218	1.11691	1.1113	1.0993	1.0864
20	1.15663	1.15254	1.14779	1.14533	1.14285	1.13774	1.13238	1.1268	1.1146	1.1017
22	1.17318	1.16891	1.16395	1.16140	1.15883	1.15358	1.14812	1.1425	1.1303	1.1172
24	1.18999	1.18557	1.18040	1.17776	1.17511	1.16971	1.16414	1.1584	1.1463	1.1331
26	1.20709	1.20254	1.19717	1.19443	1.19170	1.18614	1.18045	1.1747	1.1626	1.1492

*"International Critical Tables," Vol. III, page 79, first edition, 1928.

TABLE 165. Comparison of Commercial Caustic Soda Tests in Different Countries.

Gay-Lussac Degrees % Na₂O	Percent. Caustic % NaOH	German Degrees % Na₂CO₃	English (Newcastle) Degrees	American (New York and Liverpool) Degrees	French Degrees
59.00	76.15	100.89	59.77	60.90	93.31
59.50	76.79	101.75	60.28	61.42	94.10
60.00	77.44	102.60	60.79	61.94	94.89
60.50	78.08	103.46	61.30	62.45	95.68
61.00	78.73	104.31	61.80	62.97	96.47
61.50	79.37	105.17	62.31	63.48	97.26
62.00	80.02	106.02	62.82	64.00	98.05
62.50	80.67	106.88	63.32	64.52	98.85
63.00	81.31	107.73	63.83	65.03	99.62
63.50	81.96	108.59	64.33	65.55	100.43
64.00	82.60	109.44	64.84	66.06	101.22
64.50	83.25	110.30	65.35	66.58	102.01
65.00	83.89	111.15	65.85	67.10	102.80
65.50	84.54	112.01	66.36	67.61	103.59
66.00	85.18	112.86	66.87	68.13	104.38
66.50	85.83	113.72	67.37	68.65	105.17
67.00	86.47	114.57	67.88	69.16	105.96
67.50	87.12	115.43	68.39	69.68	106.76
68.00	87.76	116.28	68.89	70.19	107.55
68.50	88.41	117.14	69.40	70.71	108.34
69.00	89.05	117.99	69.91	71.23	109.13
69.50	89.70	118.85	70.41	71.74	109.92
70.00	90.35	119.70	70.92	72.26	110.71
70.50	90.99	120.56	71.43	72.77	111.50
71.00	91.64	121.41	71.93	73.29	112.29
71.50	92.28	122.27	72.44	73.81	113.08
72.00	92.93	123.12	72.95	74.32	113.87
72.50	93.57	123.98	73.45	74.84	114.67
73.00	94.22	124.83	73.96	75.35	115.46
73.50	94.86	125.69	74.47	75.87	116.25
74.00	95.51	126.54	74.97	76.39	117.04
74.50	96.15	127.40	75.48	76.90	117.83
75.00	96.80	128.25	75.99	77.42	118.62
75.50	97.44	129.11	76.49	77.94	119.41
76.00	98.09	129.96	77.00	78.45	120.20
76.50	98.73	130.82	77.51	78.97	120.99
77.00	99.38	131.67	78.01	79.48	121.78
77.50	100.02	132.53	78.52	80.00	122.58

TABLE 166. Specific Gravity of Dilute Sodium Carbonate Solution at 15° C. (Lunge and Wegscheider.)

Baumé Degrees	Specific Gravity	Per Cent Na₂CO₃	Baumé Degrees	Specific Gravity	Per Cent Na₂CO₃
1	1.007	0.63	11	1.083	7.85
2	1.014	1.29	12	1.091	8.57
3	1.021	1.91	13	1.099	9.21
4	1.029	2.83	14	1.107	9.99
5	1.036	3.42	15	1.116	10.85
6	1.043	3.94	16	1.125	11.67
7	1.051	4.83	17	1.134	12.46
8	1.059	5.55	18	1.143	13.15
9	1.067	6.36	19	1.152	14.09
10	1.075	7.08			
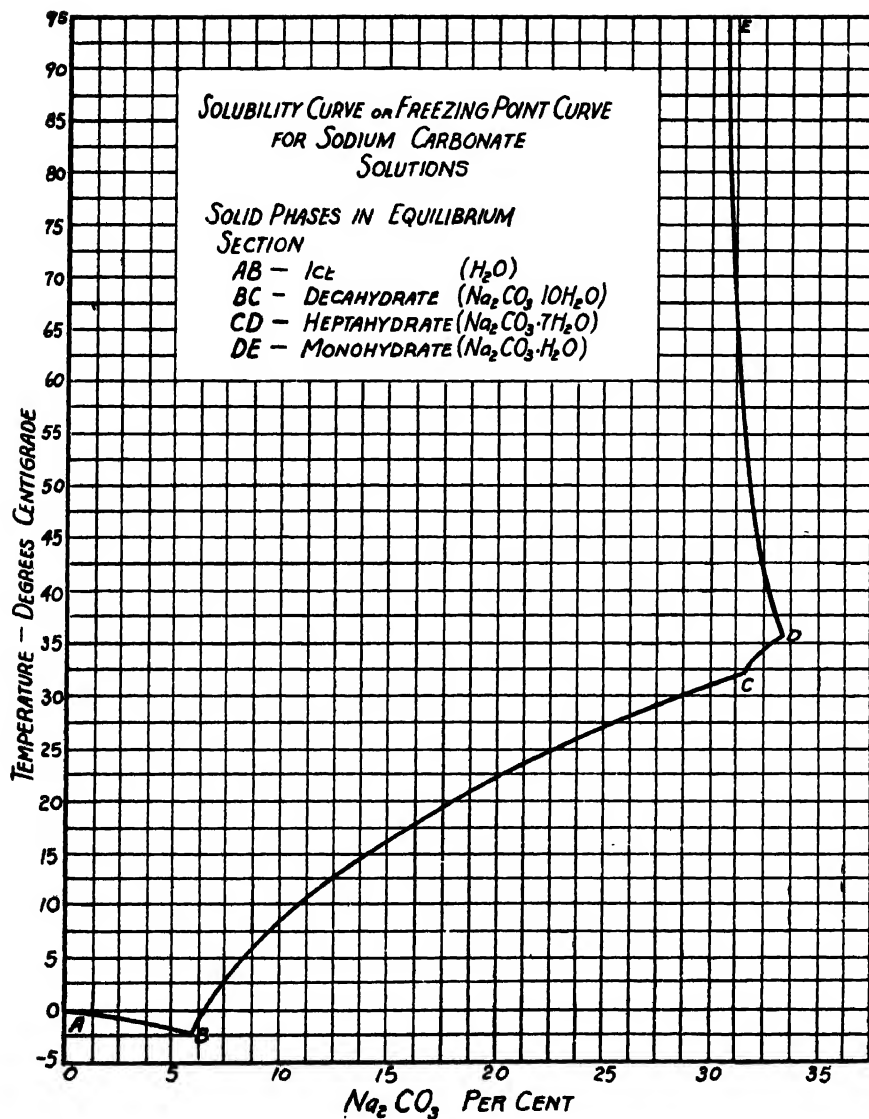
Fig. 141. Freezing point curve for sodium carbonate solutions.

TABLE 167. Specific Gravity of More Concentrated Sodium Carbonate Solut
at 30° C. (Lunge.)

Baumé Degrees	Specific Gravity	Per Cent Na_2CO_3	Baumé Degrees	Specific Gravity	Per Cent Na_2CO_3
18	1.143	13.85	27	1.230	21.53
19	1.152	14.58	28	1.241	22.34
20	1.161	15.33	29	1.252	23.18
21	1.170	16.16	30	1.263	24.10
22	1.180	17.09	31	1.274	25.10
23	1.190	18.00	32	1.285	26.00
24	1.200	18.83	33	1.297	27.00
25	1.210	19.67	34	1.308	27.90
26	1.220	20.55			

TABLE 168. Reduction of Specific Gravity of Sodium Carbonate Solution to 15° C.*
(Berl and Lunge.)

Sp. Gr. Reading	Temperature ° C. at Which the Reading is Taken										
	0	10	20	30	40	50	60	70	80	90	100
1.32	....	....	....	1.329	1.338	1.346	1.351	....	....	....	....
1.31	....	....	....	1.319	1.328	1.336	1.341	1.348	1.355	....	....
1.30	....	....	....	1.309	1.317	1.325	1.330	1.338	1.345	1.352	1.358
1.29	....	....	....	1.299	1.307	1.315	1.320	1.327	1.334	1.342	1.348
1.28	....	....	....	1.289	1.297	1.304	1.310	1.317	1.324	1.331	1.338
1.27	....	....	....	1.279	1.287	1.294	1.300	1.306	1.313	1.321	1.327
1.26	....	....	....	1.269	1.276	1.284	1.289	1.296	1.303	1.311	1.317
1.25	....	....	....	1.258	1.266	1.273	1.279	1.285	1.292	1.300	1.306
1.24	....	....	....	1.248	1.256	1.263	1.268	1.275	1.282	1.290	1.296
1.23	....	....	1.232	1.238	1.245	1.252	1.258	1.265	1.271	1.279	1.285
1.22	....	....	1.222	1.228	1.235	1.242	1.247	1.254	1.261	1.269	1.275
1.21	....	....	1.212	1.218	1.224	1.231	1.237	1.244	1.251	1.258	1.264
1.20	1.193	1.197	1.202	1.208	1.214	1.221	1.227	1.233	1.240	1.248	1.254
1.19	1.183	1.187	1.192	1.197	1.204	1.210	1.216	1.223	1.230	1.237	1.243
1.18	1.173	1.177	1.182	1.187	1.193	1.200	1.206	1.212	1.219	1.227	1.233
1.17	1.163	1.167	1.172	1.177	1.183	1.190	1.196	1.202	1.209	1.216	1.222
1.16	1.154	1.157	1.162	1.167	1.172	1.179	1.185	1.191	1.198	1.205	1.212
1.15	1.144	1.147	1.152	1.157	1.162	1.168	1.175	1.181	1.188	1.195	1.201
1.14	1.134	1.138	1.142	1.147	1.152	1.158	1.164	1.170	1.177	1.184	1.191
1.13	1.124	1.128	1.132	1.137	1.142	1.148	1.154	1.160	1.167	1.174	1.180
1.12	1.115	1.118	1.122	1.126	1.131	1.137	1.143	1.150	1.156	1.163	1.170
1.11	1.105	1.108	1.112	1.116	1.121	1.127	1.133	1.139	1.146	1.153	1.159
1.10	1.095	1.098	1.102	1.106	1.111	1.116	1.122	1.129	1.135	1.142	1.148
1.09	1.085	1.088	1.092	1.096	1.101	1.106	1.112	1.118	1.125	1.131	1.138
1.08	1.075	1.078	1.082	1.086	1.090	1.095	1.101	1.108	1.114	1.121	1.127
1.07	1.066	1.068	1.072	1.076	1.080	1.085	1.091	1.097	1.104	1.111	1.117
1.06	1.056	1.058	1.062	1.065	1.070	1.074	1.081	1.087	1.093	1.100	1.106
1.05	1.046	1.048	1.051	1.055	1.059	1.064	1.070	1.076	1.083	1.089	1.096
1.04	1.037	1.039	1.041	1.045	1.049	1.054	1.060	1.066	1.072	1.079	1.085
1.03	1.028	1.029	1.031	1.035	1.039	1.043	1.049	1.056	1.062	1.068	1.075
1.02	1.018	1.019	1.021	1.025	1.028	1.033	1.039	1.045	1.051	1.058	1.064
1.01	1.009	1.010	0.011	1.015	1.018	1.023	1.028	1.035	1.041	1.047	1.053

* See "Taschenbuch für die anorganisch-chemische Grossindustrie." I Teil, by Berl and Lunge,
7 Auflage, p. 257

TABLE 169. Specific Gravity of Caustic Soda Solutions at Various Temperatures.*

Per Cent NaOH	0° C.	10° C.	15° C.	18° C.	20° C.	30° C.	40° C.	50° C.	60° C.	70° C.	80° C.	90° C.	100° C.
1	1.0124	1.0115	1.01005	1.01003	1.0095	1.0069	1.0033	0.9990	0.9941	0.9884	0.9824	0.9760	0.9693
2	1.0244	1.0230	1.02198	1.02127	1.0207	1.0177	1.0139	1.0095	1.0045	0.9989	0.9929	0.9865	0.9797
3	1.0364	1.0345	1.03322	1.03241	1.0318	1.0285	1.0246	1.0201	1.0150	1.0094	1.0035	0.9970	0.9903
4	1.0482	1.0459	1.04441	1.04349	1.0428	1.0393	1.0352	1.0305	1.0254	1.0198	1.0139	1.0075	1.0009
5	1.0598	1.0571	1.05554	1.05454	1.0538	1.0501	1.0458	1.0412	1.0359	1.0302	1.0243	1.0179	1.0115
6	1.0713	1.0683	1.06666	1.06559	1.0648	1.0609	1.0564	1.0517	1.0463	1.0407	1.0347	1.0284	1.0220
7	1.0828	1.0795	1.07777	1.07664	1.0758	1.0717	1.0672	1.0623	1.0569	1.0513	1.0453	1.0390	1.0326
8	1.0943	1.0908	1.08887	1.08769	1.0869	1.0826	1.0780	1.0730	1.0676	1.0619	1.0560	1.0497	1.0432
9	1.1057	1.1020	1.09997	1.09872	1.0979	1.0934	1.0887	1.0836	1.0782	1.0725	1.0665	1.0602	1.0537
10	1.1171	1.1132	1.11107	1.10977	1.1089	1.1043	1.0995	1.0942	1.0889	1.0831	1.0771	1.0708	1.0643
12	1.1399	1.1355	1.13327	1.13188	1.1309	1.1261	1.1210	1.1157	1.1101	1.1043	1.0983	1.0920	1.0855
14	1.1624	1.1578	1.15545	1.15400	1.1530	1.1480	1.1428	1.1373	1.1316	1.1257	1.1195	1.1132	1.1066
16	1.1849	1.1801	1.17761	1.17610	1.1751	1.1699	1.1645	1.1588	1.1531	1.1471	1.1408	1.1343	1.1277
18	1.2073	1.2023	1.19973	1.19817	1.1972	1.1918	1.1863	1.1805	1.1746	1.1685	1.1621	1.1556	1.1489
20	1.2296	1.2244	1.22183	1.22022	1.2191	1.2136	1.2079	1.2020	1.1960	1.1898	1.1833	1.1768	1.1700
22	1.2519	1.2465	1.24386	1.24220	1.2411	1.2354	1.2296	1.2236	1.2174	1.2111	1.2046	1.1980	1.1912
24	1.2741	1.2686	1.26582	1.26412	1.2629	1.2571	1.2512	1.2451	1.2388	1.2324	1.2259	1.2192	1.2124
26	1.2963	1.2906	1.2877	1.2860	1.2848	1.2789	1.2728	1.2666	1.2603	1.2538	1.2472	1.2405	1.2336
28	1.3182	1.3124	1.3094	1.3076	1.3064	1.3002	1.2942	1.2878	1.2814	1.2750	1.2682	1.2615	1.2546
30	1.3400	1.3340	1.3309	1.3290	1.3279	1.3217	1.3154	1.3090	1.3025	1.2959	1.2892	1.2824	1.2755
32	1.3614	1.3552	1.3520	1.3502	1.3490	1.3427	1.3362	1.3298	1.3232	1.3165	1.3097	1.3029	1.2960
34	1.3823	1.3760	1.3728	1.3708	1.3696	1.3632	1.3566	1.3501	1.3434	1.3367	1.3299	1.3230	1.3161
36	1.4030	1.3965	1.3933	1.3913	1.3900	1.3835	1.3768	1.3702	1.3634	1.3567	1.3498	1.3429	1.3360
38	1.4234	1.4168	1.4135	1.4115	1.4101	1.4035	1.3967	1.3900	1.3832	1.3763	1.3695	1.3626	1.3556
40	1.4435	1.4367	1.4334	1.4314	1.4300	1.4232	1.4164	1.4095	1.4027	1.3958	1.3889	1.3820	1.3750
42	1.4632	1.4561	1.4529	1.4508	1.4494	1.4425	1.4356	1.4287	1.4217	1.4148	1.4079	1.4009	1.3940
44	1.4825	1.4755	1.4720	1.4699	1.4685	1.4615	1.4545	1.4475	1.4405	1.4335	1.4266	1.4196	1.4127
46	1.5018	1.4947	1.4911	1.4890	1.4873	1.4805	1.4734	1.4663	1.4593	1.4523	1.4454	1.4384	1.4315
48	1.5210	1.5138	1.5102	1.5080	1.5065	1.4994	1.4922	1.4851	1.4781	1.4711	1.4641	1.4572	1.4503
50	1.5400	1.5326	1.5290	1.5268	1.5253	1.5181	1.5109	1.5038	1.4967	1.4897	1.4827	1.4759	1.4690

* "International Critical Tables," Vol. III, page 79, first edition, 1928.

TABLE 170. Per Cent NaOH and Specific Gravity of Caustic Soda Solutions at 60° F.

(From "International Critical Tables," Vol. 3, page 79.)

NaOH	Specific Gravity 60°/60° F.	Baumé Am. Std.	Twaddell 60° F.	% Na₂O	Gms. NaOH per Liter
1	1.012	1.65	2.30	0.77	10.11
2	1.023	3.24	4.56	1.55	20.44
3	1.034	4.78	6.81	2.32	30.99
4	1.045	6.28	9.05	3.10	41.77
5	1.056	7.74 .	11.27	3.87	52.77
6	1.067	9.17	13.50	4.65	63.99
7	1.079	10.57	15.72	5.42	75.43
8	1.000	11.94	17.94	6.20	87.09
9	1.101	13.28	20.16	6.97	98.98
10	1.112	14.59	22.38	7.75	111.1
11	1.123	15.88	24.60	8.52	123.4
12	1.134	17.15	26.82	9.30	136.1
13	1.145	18.39	29.04	10.07	148.7
14	1.156	19.60	31.26	10.85	161.7
15	1.167	20.79	33.48	11.62	174.9
16	1.178	21.96	35.69	12.40	188.4
17	1.190	23.11	37.91	13.17	`202.0
18	1.201	24.23	40.13	13.95	215.9
19	1.212	25.33	42.34	14.72	230.0
20	1.223	26.41	44.54	15.50	244.3
21	1.234	27.47	46.75	16.27	258.8
22	1.245	28.51	48.95	17.05	273.6
23	1.256	29.53	51.15	17.82	288.5
24	1.267	30.53	53.34	18.60	303.7
25	1.278	31.52	55.54	19.37	319.1
26	1.289	32.48	57.74	20.15	334.7
27	1.300	33.43	59.92	20.92	350.6
28	1.310	34.35	62.08	21.70	366.6
29	1.321	35.25	64.24	22.47	382.8
30	1.332	36.13	66.38	23.24	399.2
31	1.343	36.99	68.50	24.02	415.8
32	1.353	37.83	70.60	24.79	432.5
33	1.363	38.65	72.68	25.57	449.5
34	1.374	39.45	74.74	26.34	466.6
35	1.384	40.23	76.80	27.12	483.9
36	1.394	41.00	78.84	27.89	501.4
37	1.404	41.75	80.88	28.67	519.1
38	1.415	42.49	82.90	29.44	537.0
39	1.425	43.21	84.90	30.22	555.0
40	1.434	43.91	86.88	30.99	573.2
41	1.444	44.60	88.84	31.77	591.6
42	1.454	45.27	90.78	32.54	610.1
43	1.463	45.92	92.68	33.32	628.7
44	1.473	46.56	94.60	34.09	647.5
45	1.483	47.20	96.52	34.87	666.5
46	1.492	47.82	98.42	35.64	685.7
47	1.502	48.44	100.3	36.42	705.1
48	1.511	49.06	102.3	37.19	724.7
49	1.521	49.65	104.1	37.97	744.4
50	1.530	50.23	106.0	38.74	764.3
51	1.540	50.81	107.9	39.52	784.4
52	1.549	51.38	109.8	40.29	804.7
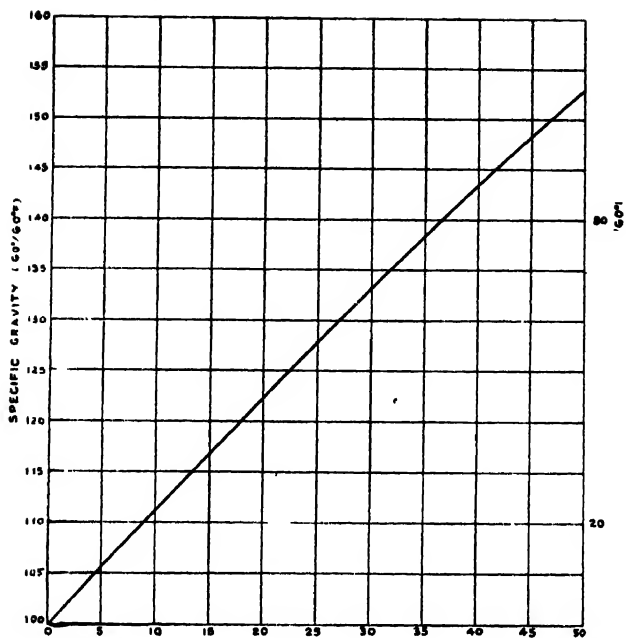
Fig. 142.   Specific gravity of caustic soda solution at 60° F.
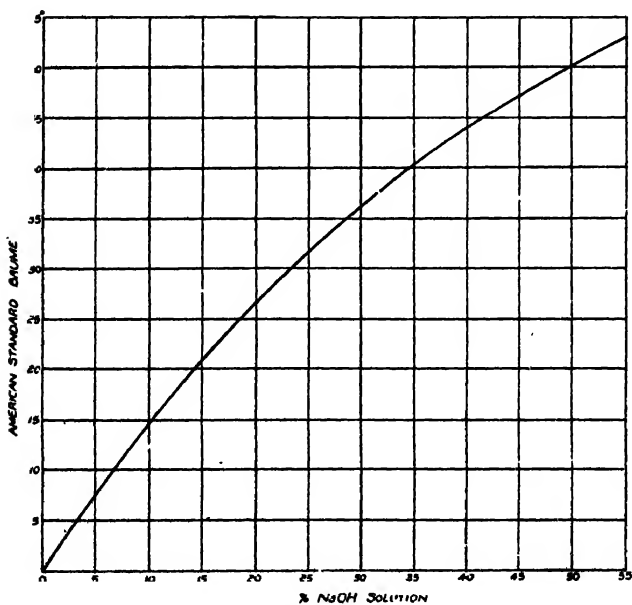
Fig. 143. , Relation between degrees Baumé of caustic soda solutions and
per cent NaOH at 60° F.

TABLE 171. Bé. Reading and Per Cei   Soda Solutions at 15° C.
                            (Lunge, Boi

Baumé Reading	Specific Gravity	Per Cent NaOH	Baumé Reading	Specific Gravity	Per Cent NaOH
1	1.007	0.59	26	1.220	19.65
2	1.014	1.20	27	1.230	20.60
3	1.021	1.77	28	1.241	21.55
4	1.029	2.50	29	1.252	22.50
5	1.036	3.15	30	1.263	23.50
6	1.043	3.65	31	1.274	24.48
7	1.051	4.40	32	1.285	25.50
8	1.059	5.11	33	1.297	26.58
9	1.067	5.86	34	1.308	27.65
10	1.075	6.58	35	1.320	28.83
11	1.083	7.30	36	1.332	30.00
12	1.091	8.07	37	1.345	31.20
13	1.099	8.71	38	1.358	32.60
14	1.107	9.42	39	1.370	33.73
15	1.116	10.30	40	1.384	35.11
16	1.125	11.06	41	1.397	36.36
17	1.134	11.90	42	1.411	37.75
18	1.143	12.59	43	1.425	39.16
19	1.152	13.50	44	1.439	40.58
20	1.161	14.24	45	1.453	42.02
21	1.170	15.06	46	1.468	43 58
22	1.180	16.00	47	1.483	45.16
23	1.190	16.91	48	1.498	46.73
24	1.200	17.81	49	1.514	48.41
25	1.210	18.71	50	1.530	50.10
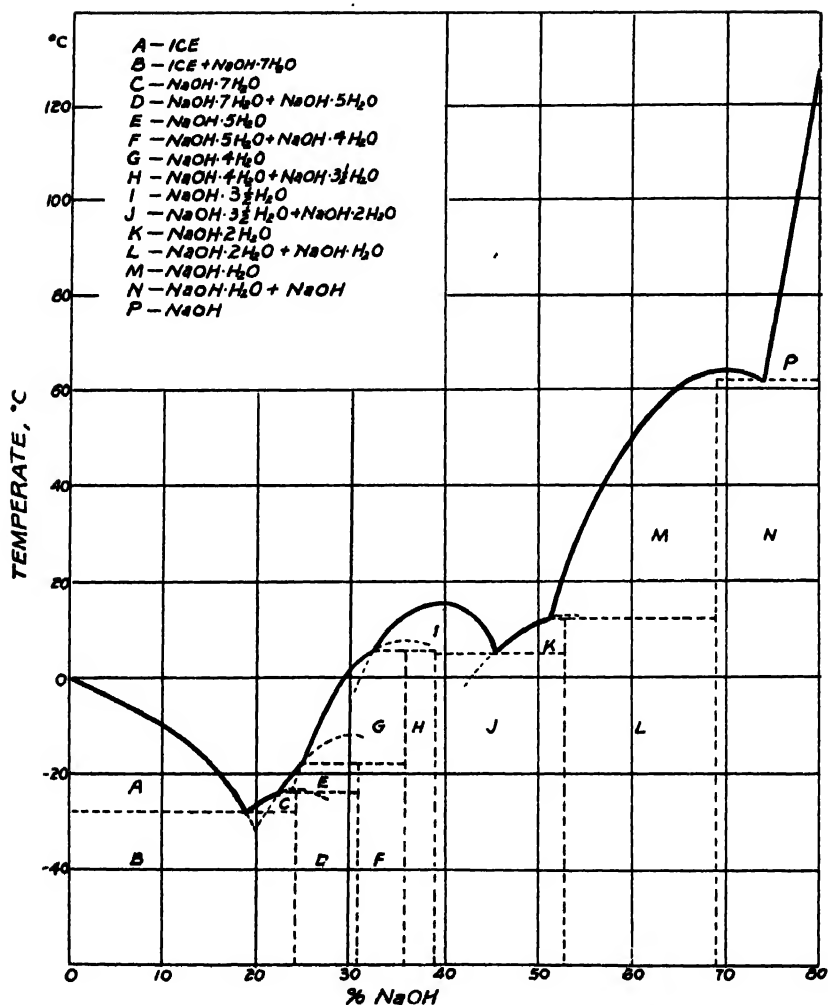
FIG. 144.   Freezing point diagram of pure NaOH and H₂O.*

* Data taken from Landolt-Börnstein, Phy. Chem. Tabellen and Pickering, Jour. Chem. Soc., 1893, Vol. 63, p. 890.

TABLE 172. Solubility of Sodium Compounds in Water at Various Temperatures.
(Lunge, Seidell, etc.)

Temperature °C.	°F.	Sodium Carbonate Na₂CO₃		Caustic Soda NaOH		Sodium Bicarbonate NaHCO₃	
		Parts per 100 Parts of Water	Na₂CO₃ by Weight Per Cent	Parts per 100 Parts of Water	NaOH by Weight Per Cent	Parts per 100 Parts of Water	NaHCO₃ by Weight Per Cent
0	32	7.0	6.5	42	29.6	6.9	6.5
5	41	9.5	8.7	48	32.0	7.5	7.0
10	50	12.5	11.1	52	34.0	8.2	7.5
15	59	16.4	14 1	...	...	8.9	8.2
20	68	21.5	17.7	109	52.2	9.6	8.8
25	77	29.8	23.0	...	...	10.4	9.4
30	86	40.9	29.0	119	54.3	11.1	10.0
35	95	51.0	33.8	...	...	11.9	10.6
40	104	49.7	33.2	129	56.3	12.7	11.3
50	122	...	...	...	...	14.5	12.6
60	140	46.4	31.7	174	63.5	16.1	14.1
80	176	45.8	31.4	313	75 8	...	...
100	212	45.5	31.3	...	...	...	...
105	221	45.2	31.1	...	...	...	...
110	230	...	...	365	78.5	...	...
192	378	...	...	521	83.9	...	...

TABLE 173. Crystallizing Temperature or Freezing Point of Sodium Hydroxide in Water. (Landolt and Börnstein.)

NaOH by Weight Per Cent	Temperat °C.	NaOH by Weight Per Cent	Tempera °C.
5.78	− 5.3	42.28	14.0
10.03	−10.3	44.22	10.7
14.11	−17.2	45.50	5.0
18.17	−25.2	47.30	7.8
19.00	−28.0	49.11	10.3
19.98	−26.0	50.80	12.3
21.10	−25.2	51.70	18.0
22.10	−24.0	56.44	40.3
23.31	−21.7	62.85	57.9
23.97	−19.5	66.45	63.2
24.70	−18.0	68.49	64.3
25.47	−12.6	71.17	63.0
26.91	− 8.5	74.20	62.0
30.38	1.6	75.83	80.0
32.30	5.4	78.15	110.0
32.97	7.0	81.09	159.0
35.51	13.2	83.87	192.0
38.83	15.6		

TABLE 174. Specific Heats of Sodium Hydroxide Solutions in Btu. per Pound per °F.

Weight Per Cent NaOH	Temperature (°F.)											
	32	40	50	60	80	100	120	140	160	180	200	300
0	1.004	1.003	1.001	0.999	0.998	0.997	0.998	0.999	1.000	1.002	1.004	....
2	0.965	0.967	0.968	0.969	0.972	0.974	0.977	0.978	0.980	0.983	0.986	....
4	0.936	0.940	0.943	0.946	0.951	0.954	0.957	0.960	0.962	0.965	0.950	....
6	0.914	0.920	0.924	0.928	0.933	0.938	0.941	0 944	0.946	0.948	0.950	....
8	0.897	0.902	0.907	0.911	0.918	0.923	0.927	0.930	0.932	0.934	0.936	....
10	0.882	0.888	0.893	0.897	0.905	0.911	0.916	0.918	0.920	0.822	0.923	....
12	0.870	0.877	0.883	0.887	0.894	0.901	0.906	0.909	0.911	0.912	0.913	....
14	0.861	0.868	0.874	0.879	0.886	0.892	0.897	0.901	0.903	0.903	0.904	....
16	0.853	0.860	0.866	0.871	0.880	0.886	0.891	0.894	0.896	0.897	0.897	....
18	0.847	0.854	0.860	0.865	0.873	0.880	0.885	0 888	0.890	0.891	0.891	....
20	0.842	0.848	0.854	0.859	0.868	0.875	0.880	0.884	0.886	0.886	0.887	....
22	0.837	0.844	0.849	0.854	0.863	0.870	0.876	0.880	0.882	0.882	0.883	....
24	....	0.839	0.844	0.849	0.858	0.866	0.873	0.877	0.879	0.879	0.880	....
26	....	0.835	0.840	0.845	0.854	0.863	0.869	0.874	0.875	0.876	0.876	....
28	....	0.830	0.836	0.841	0.850	0.859	0.866	0.870	0.872	0.872	0.873	....
30	....	0.826	0.832	0.832	0.846	0.855	0.862	0.866	0.868	0.869	0.869	....
32	....	0.822	0.828	0.833	0.842	0.850	0.857	0.862	0.863	0.864	0.864	....
34	....	....	0.823	0.828	0.837	0.845	0.852	0.856	0.857	0.858	0.858	....
36	....	....	0.819	0.824	0.832	0.840	0.845	0.849	0.850	0.851	0.851	....
38	....	....	0.816	0.820	0.827	0.833	0.837	0.841	0.842	0.842	0.843	....
40	....	....	0.812	0.815	0.821	0.826	0.829	0.831	0.832	0.832	0.832	....
42	....	....	0.807	0.809	0.813	0.816	0.819	0.819	0.820	0.820	0.820	....
44	....	....	....	0.802	0.804	0.806	0.807	0.807	0.807	0.806	0.804	....
46	....	....	....	0.793	0.794	0.795	0.794	0.794	0.793	0.791	0.789	....
48	....	....	....	....	0.783	0.782	0.781	0.780	0.779	0.777	0.776	....
50	....	....	....	....	0.771	0.769	0.768	0.767	0.765	0.765	0.764	0.761
52	....	....	....	....	0.759	0.757	0.756	0.754	0.753	0.752	0.751	0.745
54	....	....	....	....	0.746	0.744	0.741	0.739	0.739	0.738	0.737	0.728
56	....	....	....	....	0.733	0.730	0.728	0.726	0.724	0.723	0.722	0.713
58	....	....	....	....	....	0.719	0.717	0.715	0.713	0.711	0.709	0.700
60	....	....	....	....	....	0.706	0.705	0.703	0.701	0.699	0.697	0.688
62	....	....	....	....	....	....	0.694	0.692	0.960	0.688	0.687	0.677
64	....	....	....	....	....	....	0.684	0.682	0.681	0.679	0.677	0.668
66	....	....	....	....	....	....	0.675	0.673	0.671	0.669	0.668	0.658
68	....	....	....	....	....	....	....	0.663	0.662	0.660	0.658	0.649
70	....	....	....	....	....	....	....	.0655	0.653	0.651	0.649	0.640
72	....	....	....	....	....	....	....	....	0.645	0.643	0.641	0.632
74	....	....	....	....	....	....	....	....	....	0.635	0.633	0.624
76	....	....	....	....	....	....	....	....	....	0.628	0.627	0.617
78	....	....	....	....	....	....	....	....	....	....	0.620	0.611

See Bertetti and McCabe, "Specific Heat of Sodium Hydroxide Solutions," *Ind. Eng. Chem.*, **28**, 375-8 (1936) for solutions up to 50% NaOH, and McCabe and Wilson, Cooperative Investigation at the University of Michigan, for solutions from 52% to 78% NaOH.
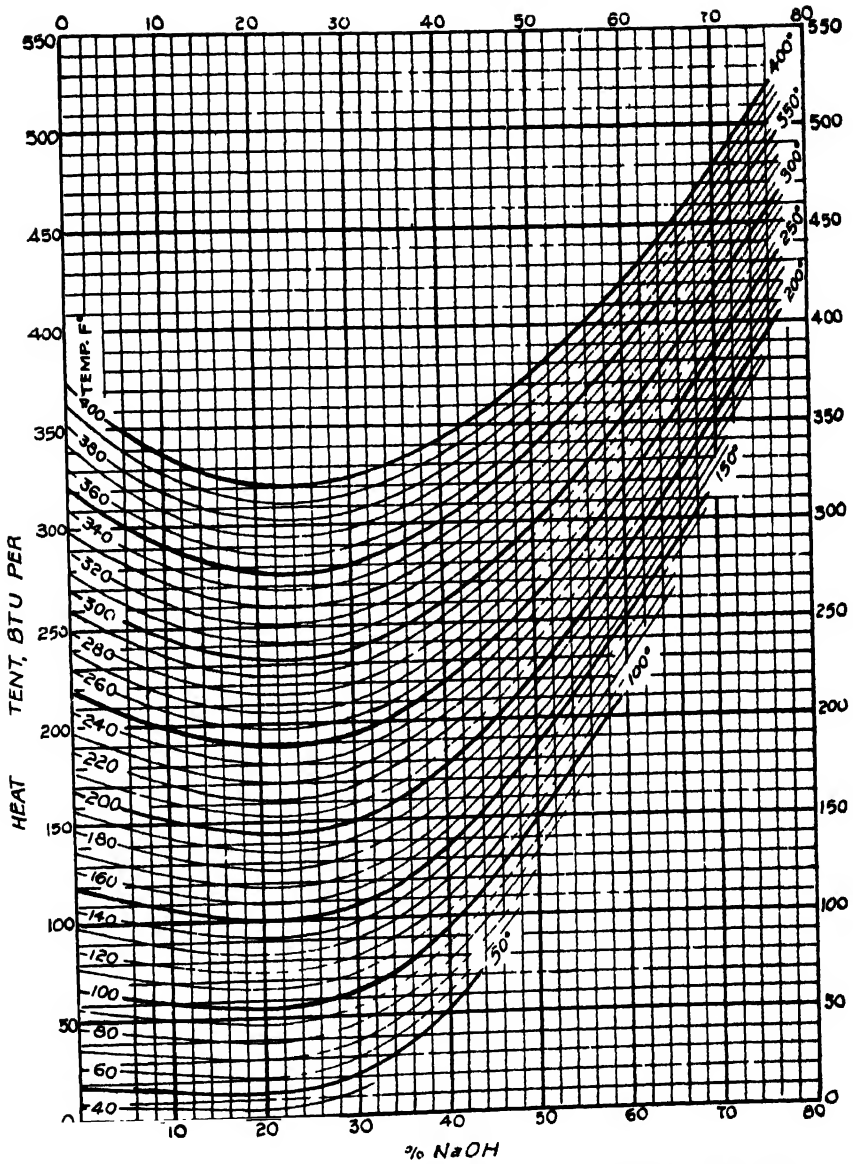
FIG. 145. Heat content-concentration chart of caustic soda solutions

The following Dühring lines * (Fig. 146) show straight-line relationship between the boiling points of caustic soda solutions and those of pure water. The figures in the right-hand margin of these lines represent
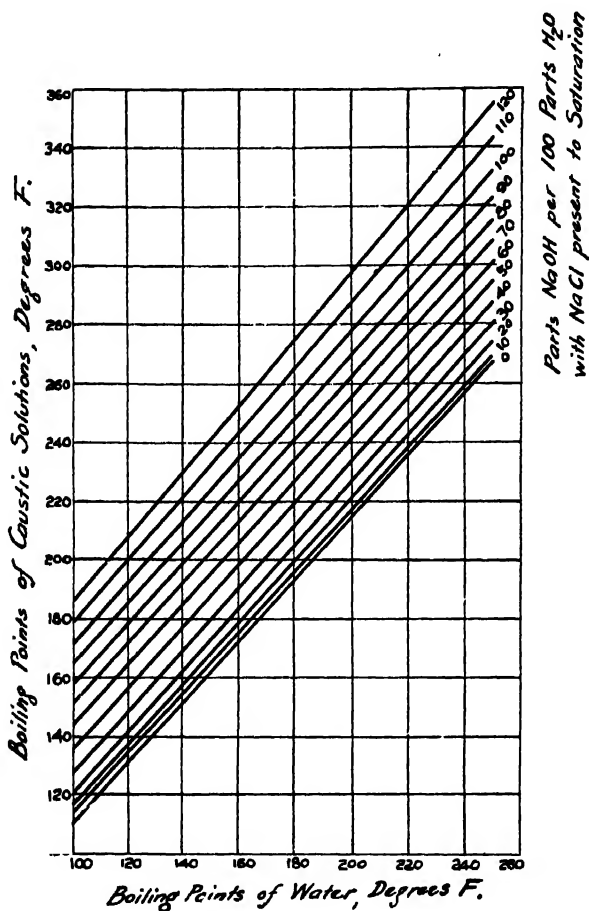
FIG. 146. Dühring lines for electrolytic caustic solutions.

parts by weight of sodium hydroxide per hundred parts of water plus the amount of salt (NaCl) held in solution up to saturation at the temperatures plotted as abscissas. The curves are especially useful in the evaporation of the electrolytic caustic liquors.

* "Boiling Points of Electrolytic Caustic Solutions" by C. C. Monrad and W. L. Badger, *Ind. Eng. Chem.*, **21**, 40 (1929). "Inorganic Chemical Technology," W. L. Badger and E. M. Baker, New York, McGraw-Hill Book Co., Inc., pp. 176-183.
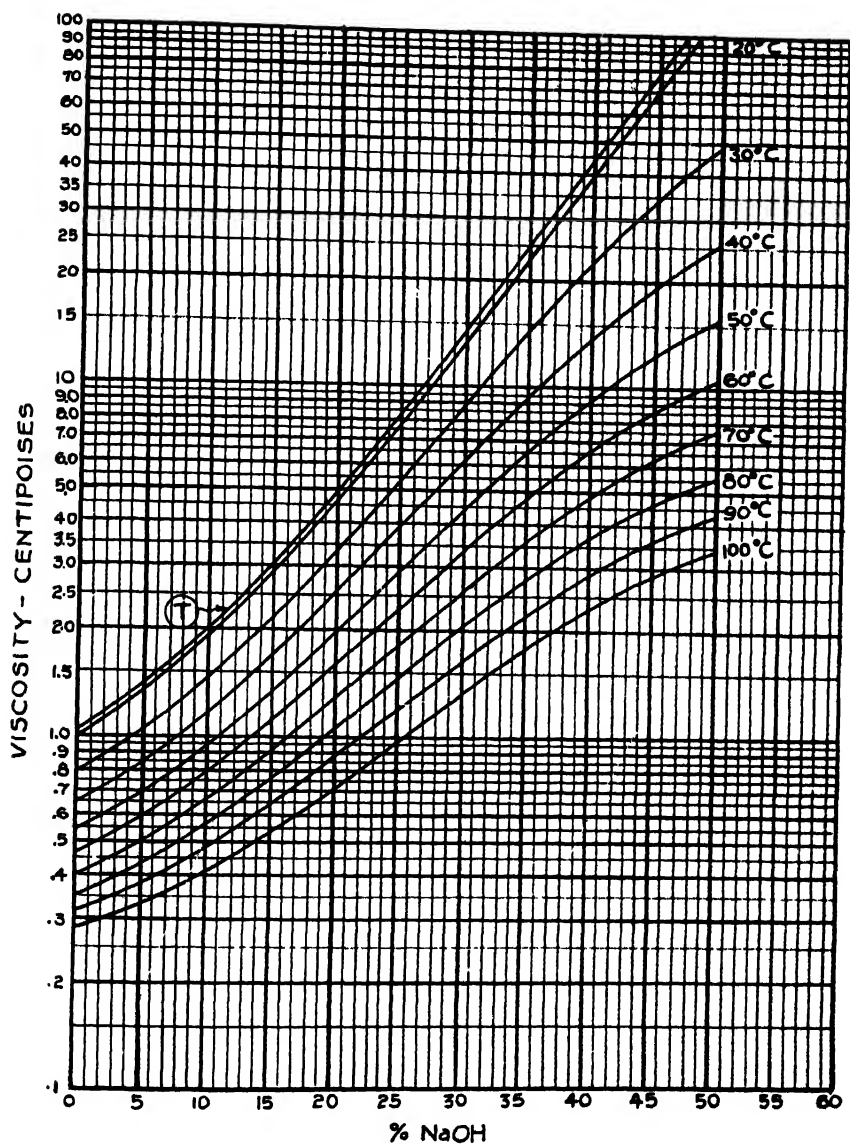
FIG. 147. Viscosity of caustic soda solutions.

TABLE 175.   Reduction of Specific Gravity of Caustic Soda Solution to 15° C.*
(Berl and Lunge.)

Sp. Gr. Reading	Temperature ° C. at Which the Reading is Taken										
	0	10	20	30	40	50	60	70	80	90	100
1.530	1.519	1.527	1.534	....	....	....	....	....	....	....	....
1.520	1.509	1.517	1.524	1.530	....	....	....	....	....	....	....
1.510	1.499	1.507	1.514	1.520	1.528	....	....	....	....	....	....
1.500	1.489	1.497	1.504	1.510	1.518	1.525	1.533	....	....	....	....
1.490	1.479	1.487	1.494	1.500	1.508	1.515	1.522	1.529	....	....	....
1.480	1.469	1.476	1.484	1.490	1.498	1.505	1.512	1.519	1.526	1.533	....
1.470	1.459	1.466	1.473	1.480	1.488	1.495	1.502	1.509	1.516	1.523	1.530
1.460	1.449	1.456	1.463	1.470	1.478	1.485	1.492	1.499	1.506	1.513	1.520
1.450	1.439	1.446	1.453	1.460	1.467	1.474	1.481	1.489	1.496	1.503	1.510
1.440	1.429	1.436	1.443	1.450	1.457	1.464	1.471	1.478	1.485	1.493	1.499
1.430	1.419	1.426	1.433	1.440	1.447	1.454	1.461	1.468	1.475	1.482	1.489
1.420	1.410	1.416	1.423	1.430	1.437	1.444	1.450	1.458	1.465	1.472	1.479
1.410	1.400	1.406	1.413	1.420	1.427	1.434	1.440	1.448	1.454	1.462	1.469
1.400	1.390	1.396	1.403	1.410	1.416	1.423	1.430	1.438	1.444	1.452	1.458
1.390	1.380	1.386	1.393	1.400	1.406	1.413	1.420	1.427	1.434	1.441	1.448
1.380	1.370	1.376	1.383	1.390	1.396	1.403	1.410	1.417	1.424	1.431	1.438
1.370	1.360	1.366	1.373	1.379	1.386	1.393	1.400	1.407	1.413	1.421	1.428
1.360	1.351	1.356	1.363	1.369	1.376	1.383	1.389	1.396	1.403	1.410	1.417
1.350	1.341	1.346	1.353	1.359	1.365	1.372	1.379	1.386	1.393	1.400	1.407
1.340	1.331	1.336	1.343	1.349	1.355	1.362	1.369	1.376	1.383	1.390	1.397
1.330	1.321	1.327	1.333	1.339	1.345	1.352	1.359	1.366	1.372	1.380	1.387
1.320	1.311	1.317	1.323	1.329	1.335	1.342	1.348	1.355	1.362	1.369	1.376
1.310	1.301	1.307	1.313	1.319	1.325	1.332	1.338	1.345	1.352	1.359	1.366
1.300	1.291	1.297	1.303	1.309	1.315	1.321	1.328	1.334	1.342	1.349	1.355
1.290	1.281	1.287	1.293	1.299	1.305	1.311	1.317	1.324	1.331	1.338	1.345
1.280	1.271	1.277	1.283	1.289	1.295	1.301	1.307	1.314	1.321	1.328	1.335
1.270	1.261	1.267	1.273	1.279	1.285	1.291	1.297	1.304	1.311	1.318	1.324
1.260	1.251	1.257	1.263	1.268	1.275	1.281	1.287	1.294	1.300	1.307	1.314
1.250	1.242	1.247	1.253	1.258	1.264	1.270	1.277	1.284	1.290	1.297	1.304
1.240	1.232	1.237	1.242	1.248	1.254	1.260	1.267	1.273	1.280	1.287	1.293
1.230	1.222	1.227	1.232	1.238	1.244	1.250	1.256	1.263	1.269	1.276	1.283
1.220	1.212	1.217	1.222	1.228	1.234	1.240	1.246	1.253	1.259	1.266	1.273
1.210	1.202	1.207	1.212	1.218	1.223	1.230	1.236	1.242	1.249	1.256	1.263
1.200	1.192	1.197	1.202	1.208	1.213	1.219	1.226	1.232	1.238	1.245	1.252
1.190	1.182	1.187	1.192	1.198	1.203	1.209	1.215	1.221	1.228	1.235	1.242
1.180	1.173	1.177	1.182	1.188	1.193	1.199	1.205	1.211	1.218	1.227	1.231
1.170	1.163	1.167	1.172	1.177	1.183	1.189	1.195	1.201	1.207	1.214	1.221
1.160	1.153	1.157	1.162	1.167	1.173	1.178	1.184	1.190	1.197	1.204	1.211
1.150	1.143	1.148	1.152	1.157	1.162	1.168	1.174	1.180	1.186	1.193	1.200
1.140	1.133	1.138	1.142	1.147	1.152	1.158	1.164	1.170	1.176	1.183	1.190
1.130	1.123	1.128	1.132	1.137	1.142	1.147	1.153	1.159	1.166	1.173	1.179
1.120	1.114	1.118	1.122	1.126	1.132	1.137	1.143	1.149	1.155	1.163	1.168
1.110	1.104	1.108	1.112	1.116	1.121	1.127	1.133	1.139	1.145	1.152	1.158
1.100	1.094	1.098	1.102	1.106	1.111	1.117	1.123	1.129	1.135	1.142	1.148
1.090	1.085	1.088	1.092	1.096	1.101	1.106	1.112	1.118	1.124	1.131	1.137
1.080	1.075	1.078	1.082	1.086	1.091	1.095	1.101	1.108	1.114	1.121	1.127
1.070	1.065	1.068	1.072	1.076	1.080	1.085	1.091	1.097	1.103	1.110	1.116
1.060	1.055	1.058	1.062	1.065	1.070	1.075	1.081	1.087	1.093	1.100	1.106
1.050	1.046	1.048	1.052	1.055	1.060	1.064	1.070	1.076	1.082	1.089	1.096
1.040	1.036	1.039	1.042	1.045	1.049	1.054	1.060	1.065	1.072	1.079	1.085
1.030	1.027	1.029	1.032	1.035	1.039	1.043	1.049	1.054	1.062	1.068	1.074
1.020	1.017	1.019	1.021	1.024	1.028	1.033	1.039	1.044	1.051	1.058	1.064
1.010	1.008	1.009	1.011	1.014	1.018	1.022	1.028	1.033	1.040	1.047	1.054

* See "Taschenbuch für die anorganisch-chemische Grossindustrie," I Teil, by Berl and Lunge, 7 Auflage, p. 257.

TABLE 176. Specific Gravity of Sodium Bicarbonate Solution at 50° C.*

NaHCO₃ by Weight Per Cent	Specific Gravity	NaHCO₃ by Weight Per Cent	Specific Gravity
1	1.006	8	1.055
2	1.013	9	1.062
3	1.020	10	1.069
4	1.027	11	1.077
5	1.034	12	1.084
6	1.041	13	1.091
7	1.048	14	1.098

* *See* "Diamond Alkali Handbook," Second Edition.
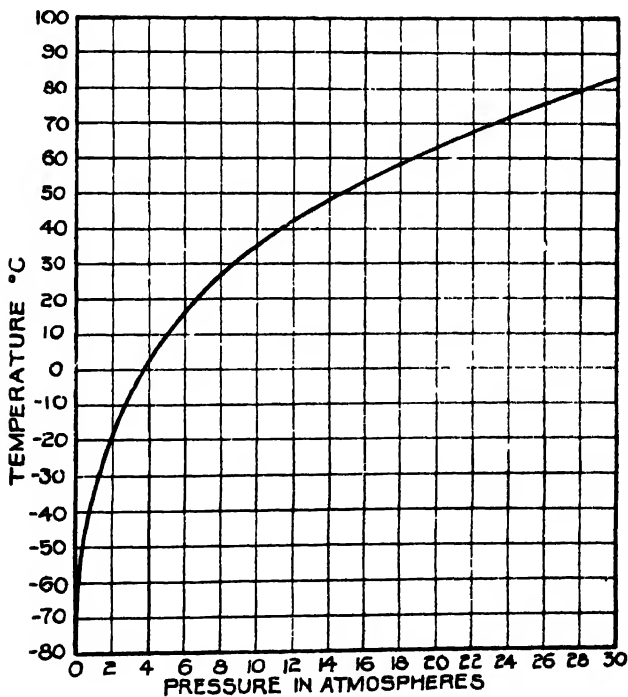
FIG. 148. Vapor pressure curve of liquid chlorine.

TABLE 177. Properties of Calcium Chloride Solution.

Pure CaCl₂ % By Weight	Specific Gravity 60° F./39° F.	Baumé Density 60° F.	Deg. Salometer 60°/60° F.	Specific Heat 60° F. B.t.u./Lb./° F.	Freezing Point ° F.	Corres. Ammonia Back Pres. Lbs./Sq. In. Ga.	Weight Per Cubic Foot		
							CaCl₂ Lbs./Cu. Ft.	Water Lbs./Cu. Ft.	Brine Lbs./Cu. Ft.
0	1.000	0.0	0.0	1.0000	32.0	47.6	0.00	62.40	62.40
5	1.044	6.1	24.4	0.9246	29.0	43.8	3.26	61.89	65.15
6	1.050	7.0	28.0	0.9143	28.0	42.6	3.93	61.59	65.52
7	1.060	8.2	32.8	0.8984	27.0	41.4	4.63	61.51	66.14
8	1.069	9.3	37.2	0.8842	25.5	39.0	5.34	61.36	66.70
9	1.078	10.4	41.6	0.8699	24.0	37.9	6.05	61.22	67.27
10	1.087	11.6	46.4	0.8556	23.0	36.8	6.78	61.05	67.83
11	1.096	12.6	50.4	0.8429	21.5	35.0	7.52	60.81	68.33
12	1.105	13.8	55.2	0.8284	19.0	32.5	8.27	60.68	68.95
13	1.114	14.8	59.2	0.8166	17.0	30.4	9.04	60.47	69.51
14	1.124	15.9	63.6	0.8043	14.5	28.0	9.81	60.27	70.08
15	1.133	16.9	67.6	0.7930	12.5	26.0	10.60	60.04	70.64
16	1.143	18.0	72.0	0.7798	9.5	23.4	11.40	59.86	71.26
17	1.152	19.1	76.4	0.7672	6.5	20.8	12.22	59.67	71.89
18	1.162	20.2	80.8	0.7566	+3.0	18.0	13.05	59.46	72.51
19	1.172	21.3	85.2	0.7460	0.0	15.7	13.90	59.23	73.13
20	1.182	22.1	88.4	0.7375	−3.0	13.6	14.73	58.90	73.63
21	1.192	23.0	92.0	0.7290	−5.5	11.9	15.58	58.61	74.19
22	1.202	24.4	97.6	0.7168	−10.5	8.8	16.50	58.50	75.00
23	1.212	25.5	102.0	0.7076	−15.5	5.9	17.40	58.23	75.63
24	1.223	26.4	105.5	0.6979	−20.5	3.4	18.32	58.00	76.32
25	1.233	27.4	109.5	0.6899	−25.0	1.3	19.24	57.70	76.94
26	1.244	28.3	113.2	0.6820	−30.0	1.6	20.17	57.39	77.56
27	1.254	29.3	117.2	0.6735	−36.0	6.1	21.13	57.12	78.25
28	1.265	30.4	121.6	0.6657	−43.5	10.6	22.10	56.84	78.94
29	1.276	31.4	125.6	0.6584	−53.0	15.7	23.09	56.53	79.62
29.5	1.280	31.7	126.8	0.6557	−58.0	17.8	23.56	56.31	79.87

TABLE 178.   Density and Vapor Pressure of Liquid Chlorine at Various Temperatures.*

Temperature °C.	Density	Vapor Pressure Mm. Hg.	Temperature °C.	Density	Vapor Pressure Atm.
−80	1.6602	62.5	−15	1.5100	2.23
−75	1.6490	88.0	−10	1.4965	2.63
−70	1.6382	118	− 5	1.4830	3.14
−65	1.6273	159	0	1.4690	3.66
−60	1.6167	210	+ 5	1.4548	4.25
−55	1.6055	275	10	1.4405	4.95
−50	1.5945	350	15	1.4273	5.75
−45	1.5830	445	20	1.4118	6.62
−40	1.5720	560	25	1.3984	7.63
−35	1.5589	705	30	1.3815	8.75
−33.6	1.5575	760	35	1.3683	9.95
			40	1.3510	11.50
		Atm.	50	1.3170	14.70
−30	1.5485	1.20	60	1.2830	18.60
−25	1.5358	1.50	70	1.2430	23.00
−20	1.5230	1.84	80	1.2000	28.40

* *See* R. Knietsch, *Ann. Chem.*, No. 259, p. 100.

TABLE 179.   Code Letters for Certain Pieces of Equipment in Solvay Works Parlance.

AB or ST—Absorber

ABR—Absorber Cooler

ABW or STW—Absorber Washer

BL—Packing Silo

CB—Cleaning Tower

CBR—Soda Decomposer for Wet Calcination

CCS—Caustic Soda Causticizer

CD—Condenser

CL—Making Tower

CLW or LCL—Tower Washer

DO or KL—Ammoniated Brine Setting Vat

DS—Distiller

DSG or DSWL—Weak Liquor Still

ED or DSHT—Distiller Blowoff Flash Tank

EG or RH or SBRH—Distiller Heater for Free Ammonia

EGV—Heater Cooler Using Liquor (Heat Exchanger)

FLR—Continuous Rotary Filter

FLRW or LVFLR or LAB—Filter Washer

KAS—Absorber Cooler

LFR—Kiln Gas Scrubber

LGS—Furnace Gas Washer

MLT—Lime Slaker

MLR—Milk of Lime Reservoir

PCB—Preliminary Absorber with Cooling Coils

PLM or MG—Prelimer

RC—Rotary Cooler

RF—Ammoniated Brine Cooler

RGRH—Distiller Condenser

RGS—Furnace Gas Condenser

RHCD—Distiller Condenser Using Liquor

SET—Settler

SB—Gas Scrubber

SP—Separator for Compressor

SHT—Rotary Dryer

SLK—Lime Kiln

TVD—Trump Vertical Dryer

TEJ—Jacket Evaporator for High Pressure Steam

TFT—Trump Feed Table

TABLE 180.   Properties of Ammonia.*

Temper-ature °F.	Pressure, Lbs. per Sq. Inch Absolute	Specific Volume Cu. Ft. per Lb. Liquid	Specific Volume Cu. Ft. per Lb. Vapor	Total Heat of Liquid	Latent Heat of Evapo-ration	Total Heat of Vapor	Entropy Liquid	Entropy Evap.	Entropy Vapor
−40	10.41	0.02322	24.84	0.0	597.0	597.0	0.000	1.423	1.423
−35	12.05	0.02333	21.66	5.3	593.6	598.9	0.013	1.398	1.411
−30	13.91	0.02345	18.96	10.7	590.2	600.9	0.025	1.374	1.399
−25	15.98	0.02357	16.64	16.0	586.8	602.8	0.037	1.350	1.387
−20	18.30	0.02369	14.67	21.4	583.3	604.7	0.050	1.327	1.377
−15	20.88	0.02381	12.97	26.7	579.7	606.4	0.062	1.304	1.366
−10	23.75	0.02393	11.50	32.1	576.1	608.2	0.074	1.281	1.355
−5	26.92	0.02406	10.22	37.5	572.4	609.9	0.086	1.259	1.345
0	30.42	0.02419	9.114	42.9	568.7	611.6	0.097	1.237	1.334
5	34.28	0.02432	8.149	48.3	564.9	613.2	0.109	1.216	1.325
10	38.51	0.02446	7.304	53.8	561.0	614.8	0.121	1.195	1.316
15	43.15	0.02460	6.562	59.2	557.1	616.3	0.132	1.174	1.306
20	48.21	0.02474	5.910	64.7	553.1	617.8	0.144	1.153	1.297
25	53.73	0.02488	5.336	70.2	549.1	619.3	0.155	1.133	1.288
30	59.74	0.02503	4.827	75.7	544.9	620.6	0.166	1.113	1.279
35	66.26	0.02518	4.375	81.2	540.7	621.9	0.177	1.093	1.270
40	73.32	0.02533	3.974	86.8	536.5	623.3	0.189	1.074	1.263
45	80.95	0.02548	3.616	92.3	532.1	624.4	0.200	1.054	1.254
50	89.19	0.02564	3.296	97.9	527.7	625.6	0.211	1.036	1.247
55	98.05	0.02581	3.010	103.5	523.1	626.6	0.221	1.017	1.238
60	107.6	0.02597	2.754	109.2	518.5	627.7	0.232	0.998	1.230
65	117.8	0.02614	2.522	114.8	513.7	628.5	0.243	0.979	1.222
70	128.8	0.02632	2.314	120.5	508.9	629.4	0.254	0.961	1.215
75	140.5	0.02650	2.126	126.2	504.1	630.3	0.264	0.943	1.207
80	153.1	0.02668	1.956	132.0	499.1	631.1	0.275	0.925	1.200
85	166.4	0.02687	1.803	137.7	494.0	631.7	0.285	0.907	1.192
90	180.7	0.02707	1.663	143.5	488.8	632.3	0.296	0.889	1.185
95	195.8	0.02727	1.536	149.3	483.5	632.8	0.306	0.872	1.178
100	211.9	0.02747	1.419	155.2	478.0	633.2	0.316	0.854	1.170
105	228.9	0.02769	1.314	161.1	472.5	633.6	0.327	0.837	1.164
110	247.0	0.02790	1.217	167.0	466.7	633.7	0.337	0.819	1.156
115	266.1	0.02813	1.129	173.0	460.9	633.9	0.347	0.802	1.149
120	286.4	0.02836	1.048	179.0	454.9	633.9	0.358	0.785	1.143

* U. S. Bureau of Standards.
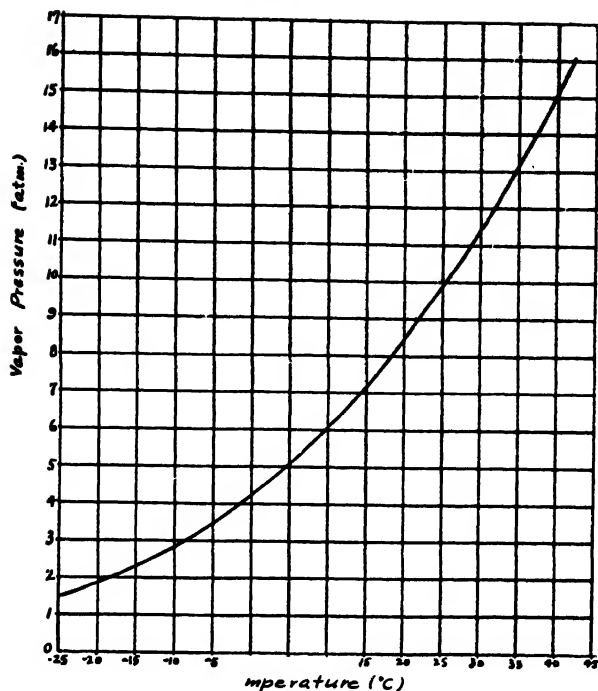
Fig. 149. Vapor pressure of liquid ammonia.

TABLE 181. Heat Capacity (Cp) of Liquid Ammonia (joules per gram).*

Temperature °C.	Cp of Liquid NH$_3$ joules/gram	Temperatu °C.	Cp of Liquid NH$_3$ joules/gram
−60	4.383	60	5.084
−40	4.440	80	5.42
−20	4.510	90	5.71
0	4.597	100	6.19
+20	4.710	110	6.72
40	4.860		

"International Critical Tables," Page 114. Vol. V. (4.183 joules = 1 gram calorie).

TABLE 182. Heat Capacity (Cp) of Gaseous Ammonia (joules per gram).*

t °C Patm.	0	1	2	4	8	12	16	20
Satd.		2.34$_0$	2.48$_3$	2.70$_1$	3.03$_0$	3.30$_0$	3.56$_1$	3.84$_2$
−30	2.02$_0$	2.30$_6$						
−10	2.04$_3$	2.19$_5$	2.38$_6$					
0	2.05$_7$	2.17$_3$	2.31$_4$	2.65$_7$				
+20	2.08$_6$	2.15$_9$	2.24$_4$	2.44$_6$	2.98$_8$			
40	2.11$_6$	2.16$_7$	2.25$_2$	2.35$_0$	2.66$_0$	3.07$_3$		
60	2.14$_9$	2.18$_6$	2.22$_6$	2.31$_5$	2.51$_2$	2.75$_9$	3.05$_6$	3.44$_6$
80	2.18$_4$	2.21$_2$	2.24$_2$	2.30$_5$	2.44$_5$	2.60$_5$	2.78$_9$	3.00$_6$
100	2.22$_0$	2.21$_4$	2.26$_5$	2.31$_5$	2.41$_5$	2.52$_6$	2.65$_2$	2.79$_2$
120	2.25$_6$	2.27$_4$	2.29$_3$	2.33$_0$	2.40$_0$	2.49$_2$	2.58$_5$	2.67$_6$
150	2.29$_4$	2.32$_7$	2.34$_0$	2.36$_8$	2.42$_2$	2.48$_1$	2.54$_9$	2.60$_5$

* "International Critical Tables," Page 83, Vol. V.

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